

WARM WASTE POND BENCH-SCALE TREATABILITY STUDY

**Submitted to:
ASI, Inc.
Idaho Falls, ID**

SEPTEMBER 1992





September 21, 1992

Mr. Walter N. Sato
U.S. Department of Energy
Idaho Operations Office
785 DOE Place
Idaho Falls, ID 83402

SUBJECT: Transmittal of Laboratory Results - Test Reactor Area Warm Waste Pond
Sediments

Dear Mr. Sato:

With this letter, I am transmitting a report entitled "Warm Waste Pond Bench-Scale Treatability Study" for your review and comment. Additionally, you will find a copy of the audit report, quality assurance program document, and surveillance report related to this study. These documents represent the product of ASI Task 21.03, TRA Warm Waste Pond Treatability Study. The task was assigned to ASI and its subcontractor, Nuclear Remediation Technologies Inc., in order to further examine the physical and chemical properties of cesium-137 and cobalt-60 contaminated sediments at the TRA Warm Waste Pond. The study emphasized confirmation of existing treatment-oriented knowledge and the exploration of alternative procedures for treating contaminated soils at the Warm Waste Pond.

As will be noted in the results report, a new basis has been developed for technologically addressing TRA Warm Waste Pond sediments contaminated with cesium-137 and cobalt-60. Test results suggested that a volume reduction of 90% is potentially attainable using currently available nonhazardous reagents and modular treatment processes without production of excessive secondary waste streams.

The enclosed report offers considerable physical and chemical information pertinent to the remediation of TRA Warm Waste Pond sediment remediation. These data have allowed study investigators to infer the potential effectiveness of existing treatment process options which, though beyond the scope of this task, would have bearing on future pilot-scale tests. The investigators involved in this study are available at the convenience of DOE Remedial Project Managers to explain study findings in greater detail and, if desired, to explore their possible application to field actions. If you have any questions, feel free to contact me at 529-2002.

Sincerely,

Jim B. States
Project Manager

Attachments

cc: Nolan Jensen, DOE (with 4 copies of 2 attachments)
Alice Williams (without attachments)
Lisa Green (without attachments)

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EXECUTIVE SUMMARY

A series of soil washing tests have been conducted on soil sediments from the Warm Waste Pond (WWP) within the Test Reactor Area at the Idaho National Engineering Laboratory. Although the sediments are contaminated with cesium-137, cobalt-60, and chromium, the CERCLA Record of Decision (ROD) requires only the removal of the cesium-137 down to an average level of 690 pCi/g in at least 90% of the total volume.

Nuclear Remediation Technologies, a division of General Atomics, performed tests on kilogram quantities of WWP samples in an attempt to identify alternative methods suitable for remediating the sediments. This test complimented the bulk nitric acid leaching investigations being conducted by others. The testing combined sieving, flotation, attrition scrubbing and other techniques borrowed from the mining industry, along with various reagents, some proprietary, to achieve the required contaminant reduction. The WWP ROD targeted 690 pCi/g Cesium-137 as a goal for the testing program; secondary waste stream generation was to be held to a minimum. In addition, the use of RCRA hazardous chemicals and their residuals were to be minimized to the greatest possible extent.

Tests performed on a 21.7 kg sample (Sample 1) included: 1) sample characterization (particle fraction weight percentages and contaminant concentrations, 2) sieving, 3) flotation using various frothing and collector agents, 4) attrition scrubbing with ammonium hydroxide, hydrogen peroxide and proprietary halide reagents, 5) stir washing with a variety of reagents, and 6) pyrolyzing. Radionuclides were found to be strongly associated with the organic and/or the finer fractions of the sediments. Tests were specifically designed for the removal of these contaminants from specific size fractions. Each test was performed individually to ascertain a workable combination of parameters. These processes were then combined into an integrated treatment process train such as sieving-flotation-attrition scrubbing-leaching. Mass balances and the cesium-137 and cobalt-60 contaminant concentrations were measured before, during and at

the conclusion of each test. Additional special testing of processes that could lead to enhanced and optimized contaminant reduction were examined in rudimentary form to ascertain their usefulness in future design studies.

Test results indicated that by combining selected process steps (screening, flotation, attrition scrubbing and leaching), more than 90% of the WWP sediment can be reduced to a Cs-137 concentration of 690 pCi/g or less. Successfully treated sediments could be backfilled to the pond in accordance with the separation/extraction treatment method stated by the ROD. The remaining 10% or less, containing highly concentrated cesium-137 and cobalt-60, could be disposed of as normal LLW or subjected to further treatment.

Additional sediment samples, totaling more than 80 kg. and taken from two of the three WWP cells, were examined late in the testing program. These samples had an inordinate quantity of organic material which interfered with the operation of the processes being bench-tested. However, it was determined through evaluation of previously collected WWP Characterization Data that these samples were not representative of the average contaminant concentration and organic content of the WWP. These samples were examined to determine capability to deal with these anomalies on a process specific program and to determine their effect on process stability and throughput. It appears that these irregularities could be managed in a production scale plant through thermal pre-treatment, selective excavation and/or feedstock blending.

Integrated testing suggested that the evaluated processes, when optimized, could provide a total volume reduction of greater than 90%. Application of additional treatments such as vitrification of the residual sediments has the potential to reduce temporary storage requirements to 3-5% of the original volume.

These test results do not permit definition of a comprehensive treatment process for the WWP sediments. Additional testing required to support future work on the Warm Waste Pond sediment remediation should include: (1) process definition, e.g. steps, reagents, sequence, (2) optimizing process conditions, e.g. temperature, pH, (3) definition and testing of pre-treatment

steps for organic material removal, and (4) process plant design for a full pilot-scale remediation facility.

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1.0 INTRODUCTION

The Test Reactor Area (TRA) at the Idaho National Engineering Laboratory (INEL) includes a three cell Warm Waste Pond (WWP). Large quantities (in excess of five billion gallons) of slightly radioactive waste water were discharged into the ponds over the past 40 years. The water has either evaporated or infiltrated into the ground, but much of the contaminants carried by the waste water were absorbed by pond sediments. Reference 1 includes an initial characterization of the WWP. As a result of this characterization, a decision was made to remediate the pond sediments (Ref. 2). The study reported herein was initiated to examine specific radioactive sediment contaminants, namely cesium-137 and cobalt-60. Testing for chromium was not emphasized in this study because of statements in the characterization report (Ref. 1) that all chromium in the WWP sediments was in the non-hazardous trivalent form. However, samples were collected and reserved from key process points for possible future chromium analysis.

Preliminary laboratory tests demonstrated the feasibility of remediating the sediments by first screening out the large sediment particles, followed by chemical treatment of the remaining particles. Contaminant levels of the untreated large particles contained Cs-137 and Co-60 concentrations low enough that no further treatment is necessary.

Nuclear Remediation Technologies (NRT), a division of General Atomics, was subcontracted by the Department of Energy through Advanced Sciences, Inc. (ASI) to conduct this test program. The intent of this study was to confirm previous treatment results with measurements of secondary waste generation percentages, extend and expand the knowledge of potential treatment methods and identify combined physical/chemical treatment technologies which would result in the greatest quantity of "cleaned" sediment with the smallest amount of secondary waste generated. The task also included testing bulk quantities (kilogram size) of

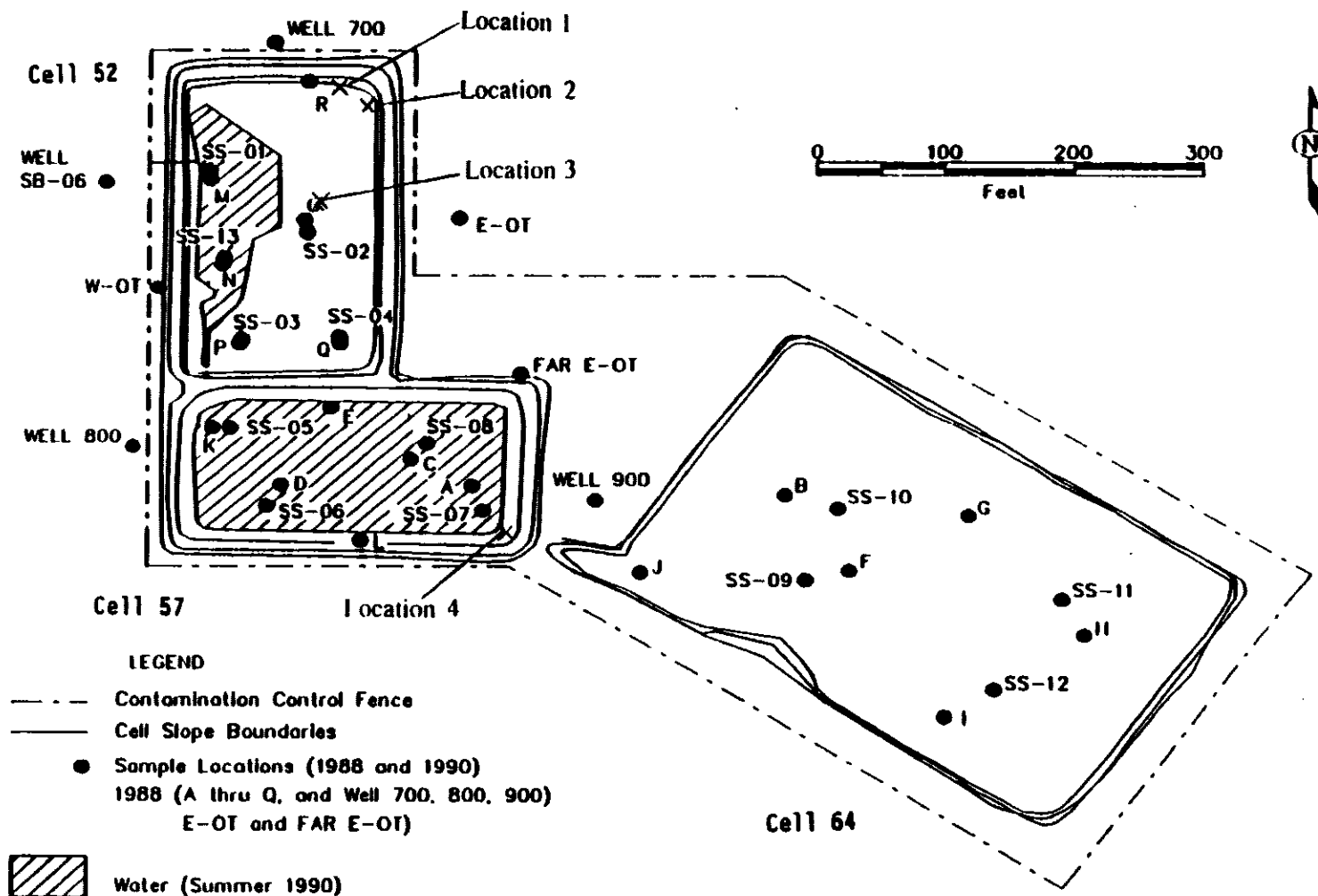
WWP samples in bench apparatus which has historically been shown to be readily up-scalable to production scale processes and has duplicated the action of full-scale production equipment.

Most testing described in Section 3.0 of this report was completed using an initial 21.7 kg WWP sediment sample, believed to have been taken from the center of Cell 52. Near completion of the test effort, additional sediment samples from several WWP locations were provided. Sampling locations are shown in Figure 1-1. The sample selected for additional testing (Location 3), although not the most radioactive of those received, had a Cs-137 concentration more than ten times the WWP average concentration quoted in the Characterization Study (Ref. 1).

The NRT test effort emphasized the reduction of the Cs-137 and Co-60 concentrations in the bulk of sediments to acceptable levels while employing methodologies which would generate the smallest amount of secondary waste and utilize reagents which were less hazardous than those used by others in previous tests. The goal for an acceptable residual average Cs-137 concentration in the bulk of the treated sediments was established at 690 pCi/g (Ref 2). The remediation testing focused on soil washing techniques to separate the more highly contaminated sediment fines and organics, while minimizing the sediment fractions requiring chemical treatment (e.g. leaching). Confirmatory testing of the ability of low pH, heated acid leaches to remove contaminants from soil samples and to measure the secondary waste generated by a previously tested screen-leach process (Ref. 3) was undertaken. Integrated tests on candidate soil washing process treatment trains were conducted in accordance with a Test Plan prepared by NRT (Ref 4).

This report contains the results of the various tests performed by NRT. It summarizes the sample characteristics and test procedures, and draws conclusions from the results. A much more detailed description of the test results, for both the first and second samples, is contained in Section 3.0 of this report. The report concludes with identification of options for future work to continue the optimization work proceeding directly to full pilot- level plant design and construction. Supporting calculations, analytical results, laboratory notebook entries, and the Material Safety Data Sheets (MSDS) for the less common treatment chemicals are published in a separate report (Ref 5).

Fig. 1-1. Sampling locations for warm waste pond sediments



2.0 SUMMARY AND CONCLUSIONS

2.1 SUMMARY

2.1.1 Approach

A great deal of work has been performed in an effort to demonstrate the effectiveness of low pH heated acids in dissolving Cs-137 and Co-60 from WWP sediments. These strong acids were shown to generate large quantities of secondary waste when neutralized.

While NRT reevaluated the problems associated with heated, low pH acid leaching of radionuclides from WWP sediments, the test approach for this study focused on combining currently available physical/chemical systems to minimize the amount of sediments requiring strong acid leaching and the use of acids treatable at the Idaho Chemical Processing Plant. The systems and reagents used were chosen on the basis of their compatibility when combined into a single optimized system custom configured for maximum Cs-137 and Co-60 removal from WWP sediments.

Key physical system components chosen included froth flotation and attrition scrubbing. Multiple "mild" reagents at various pH and solution strength combinations were examined. An example was the use of hydrogen peroxide, a strong oxidizer, which breaks down into water at a neutral pH eliminating downstream neutralization and attendant sludge generation.

2.1.2 Results

Two separate samples of Warm Waste Pond sediments were examined in the remediation R&D effort conducted by NRT. Most of the effort was expended on the first sample. The original intent was to conduct confirmatory tests using a second sample, (one of four sets of

samples) that was received after work on the first sample was completed. The two samples, however, differed significantly in radionuclide content and in radionuclide distribution among the various particle sizes. Average activity on a total sample basis for Sample 1 was 2,470 pCi Cs-137/g and 710 pCi Co-60/g versus 52,000 pCi Cs-137/g and 24,600 pCi Co-60/g for Sample 2. Tables 2-1 and 2-2 contain characterization results for Samples 1 and 2 respectively. Figure 2-1 graphically illustrates Cs-137 and Co-60 concentration and distribution differences between the two samples. Particle size distribution differences are shown in Figure 2-2. The greater organic material content of the Sample 2 (8.5% versus 0.75%) likely contributes to the higher concentration of Cs-137 (20 times higher) and Co-60 (35 times higher). The Sample 2 average Cs-137 and Co-60 concentrations are a factor of two higher than the upper bounds of the ranges for contaminant concentrations identified in Reference 1. By visual inspection, the other three batches of samples from the group of four samples gathered during the last sampling effort have significantly larger quantities of organic material than the batch selected for processing. All four batches of samples appear to be surface samples. Sample 2 was identified as Cell 52 center (Location 3 on Fig. 1-1). The origin of Sample 1 is not documented, but it is believed to a full depth range (0-24 inch) sample from the center of Cell 52.

Figure 2-3 illustrates a comparison of Samples 1 and 2 particle size distributions with average and bounding values obtained from the WWP characterization study (Ref. 1.). Sample 2 showed a marked departure (greater fines fractions) from the characterization study values. Measurement methodology differences (wet versus dry screening) could account for the disparity.

Based on a goal of achieving a residual Cs-137 concentration of less than 690 pCi/g (Ref. 2), the Sample 1 large mesh fractions (greater than 4 mesh) needed no further treatment. The corresponding Sample 2 fractions were about the same weight fraction but required treatment. Treatments attempted on Sample 2 large (+4 mesh) fractions included soaking in hot nitric acid, hot ammonium hydroxide, and MICRO® (a detergent compounded for laboratory equipment decontamination). Under the conditions tested, none of the Sample 2 treated material had residual concentrations below the goal value. Portions of the treated rocks retained coatings of dried scum assumed to contain the residual radionuclides. In a special test to examine the effect of pyrolyzing the organics, the coatings on previously untreated +4 mesh sediments were

**Table 2-1
First Sample Characterization Results**

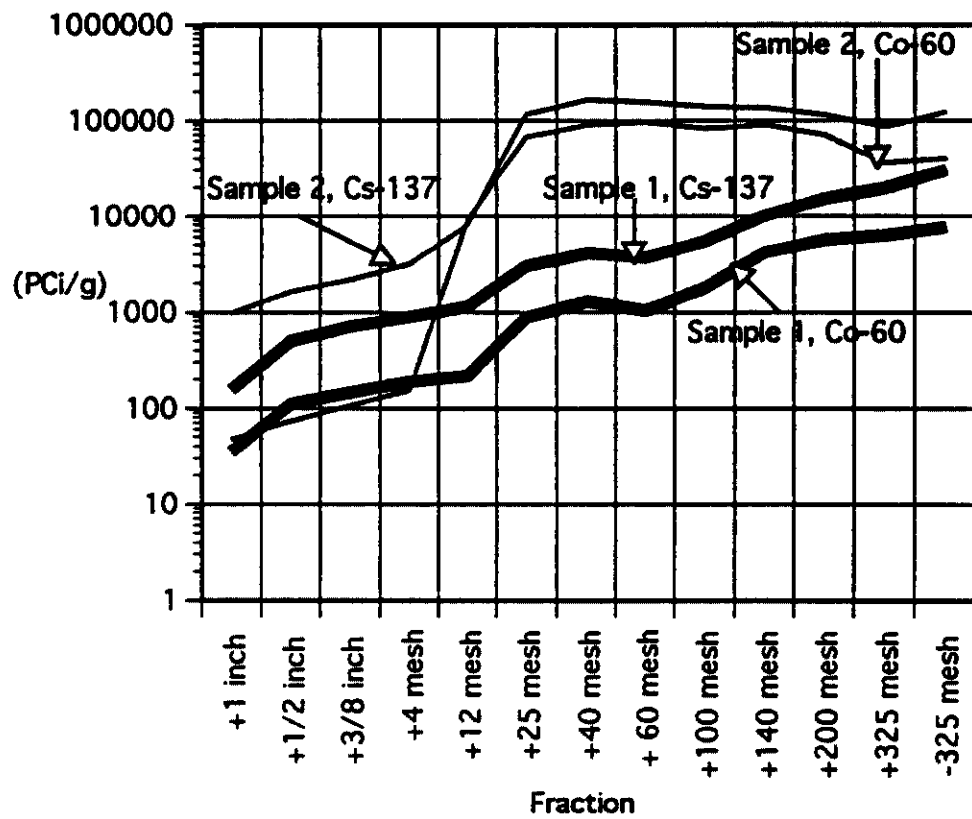
Retained Fraction	Weight, g		Analysis, pCi/g		Cumulative Average Concentration, pCi/g		Cumulative Percentages		
	Fraction	Cumulative	Cs-137	Co-60	Cs-137	Co-60	Weight	Cs-137	Co-60
1 inch	5132.0	5132.0	155	35	155	35	23.69	1.49	1.17
½ inch	2945.0	8077.0	504	112	282	63	37.29	4.25	3.32
¾ inch	1122.0	9199.0	712	146	334	73	42.47	5.73	4.38
4 mesh	2268.5	11467.5	897	191	445	97	52.95	9.53	7.20
12 mesh	1841.2	13308.7	1150	218	543	113	61.45	13.49	9.81
25 mesh	1697.2	15005.9	3020	887	823	201	69.28	23.07	19.64
40 mesh	3005.1	18011.0	4070	1290	1365	383	83.16	45.91	44.88
60 mesh	2057.9	20068.9	3710	1030	1604	449	92.66	60.15	58.67
100 mesh	807.3	20876.2	5480	1800	1753	502	96.39	68.37	68.11
140 mesh	215.8	21092.0	10200	4140	1840	539	97.38	72.38	73.90
200 mesh	94.8	21186.8	15300	5680	1902	562	97.82	75.28	77.41
325 mesh	118.7	21305.5	20000	6070	2002	593	98.37	79.67	82.22
-325 mesh	353.3	21658.8	30800	7740	2470	710	100.00	100.00	100.00

Table 2-2
Second Sample Characterization Results

Retained Fraction	Weight, g		Analysis, pCi/g		Cumulative Average Concentration, pCi/g		Cumulative Percentages			Percent ⁽¹⁾⁽²⁾ Weight Loss on Ignition
	Fraction	Cumulative	Cs-137	Co-60	Cs-137	Co-60	Weight	Cs-137	Co-60	
1 inch	651.0	651.0	979	47.2	979	47.2	24.00	0.45	0.05	
½ inch	483.3	1134.3	1,625	73.0	1,255	58.2	41.83	1.01	0.10	
¾ inch	159.0	1293.3	2,170	108	1,370	64.3	47.69	1.25	0.12	
4 mesh	213.9	1507.2	3,160	153	1,620	76.9	55.58	1.73	0.17	
12 mesh	124.2	1631.4	8,030	9,070	2,110	761	60.15	2.44	1.86	2.40
25 mesh	100.4	1731.8	117,000	67,200	8,770	4,610	63.86	10.76	11.97	22.97
40 mesh	85.9	1817.7	166,000	89,200	16,200	8,610	67.02	20.86	23.45	18.28
60 mesh	115.3	1933.0	155,000	94,800	24,500	13,750	71.28	33.52	39.83	19.21
100 mesh	101.8	2034.8	139,000	82,300	30,200	17,200	75.03	43.55	52.39	24.24
140 mesh	45.7	2080.5	136,000	89,300	32,500	18,800	76.71	47.96	58.50	21.28
200 mesh	85.5	2166.0	115,000	70,200	35,800	20,800	79.87	54.92	67.49	21.62
325 mesh	113.8	2279.8	86,300	36,400	38,300	21,600	84.06	61.88	73.70	12.87
-325 mesh	432.2	2712.0	124,500	40,600	52,000	24,600	100.00	100.00	100.00	17.09

⁽¹⁾ At 400°C overnight

⁽²⁾ The weighted ignition losses are 17% for the -4 mesh portion and > 7.57% for the entire sample
The corresponding ignition losses for the first sample are 1.59% and 0.75%



Sample 1 Avg., Cs-137	2470
Sample 2 Avg., Cs-137	52,000
Sample 1 Avg., Co-60	710
Sample 2 Avg., Co-60	24,600

Fig. 2-1. WWP sediment sample comparison – Cs-137 and Co-60 content

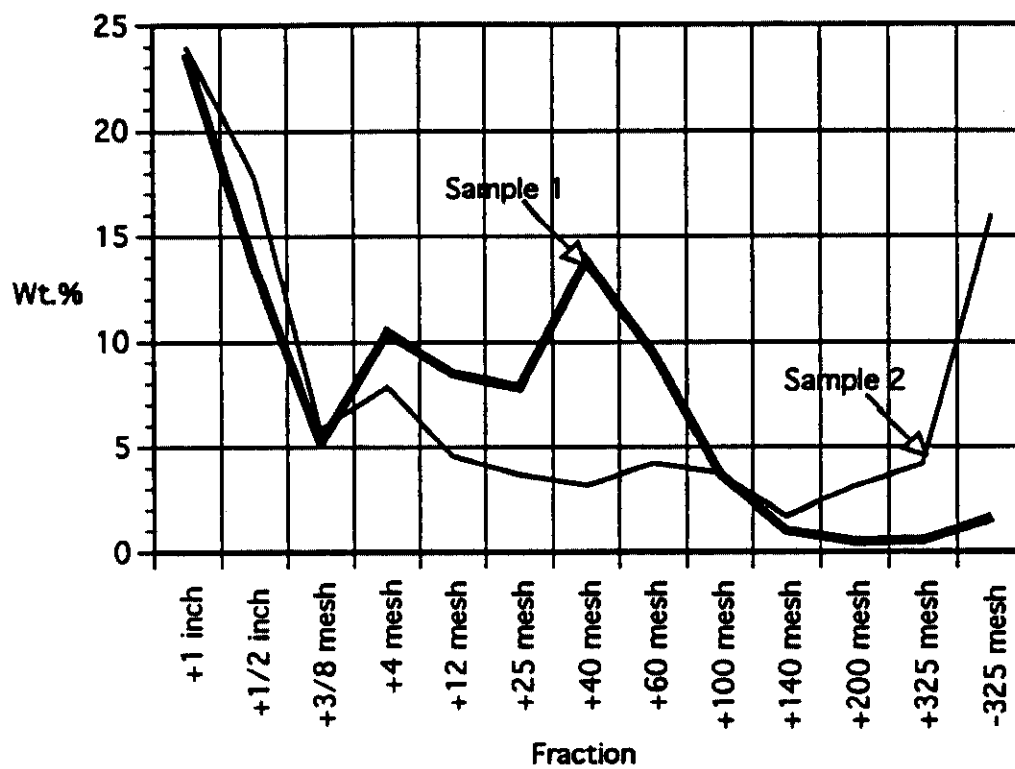


Fig. 2-2. WWP sediment sample comparison – particle size distribution

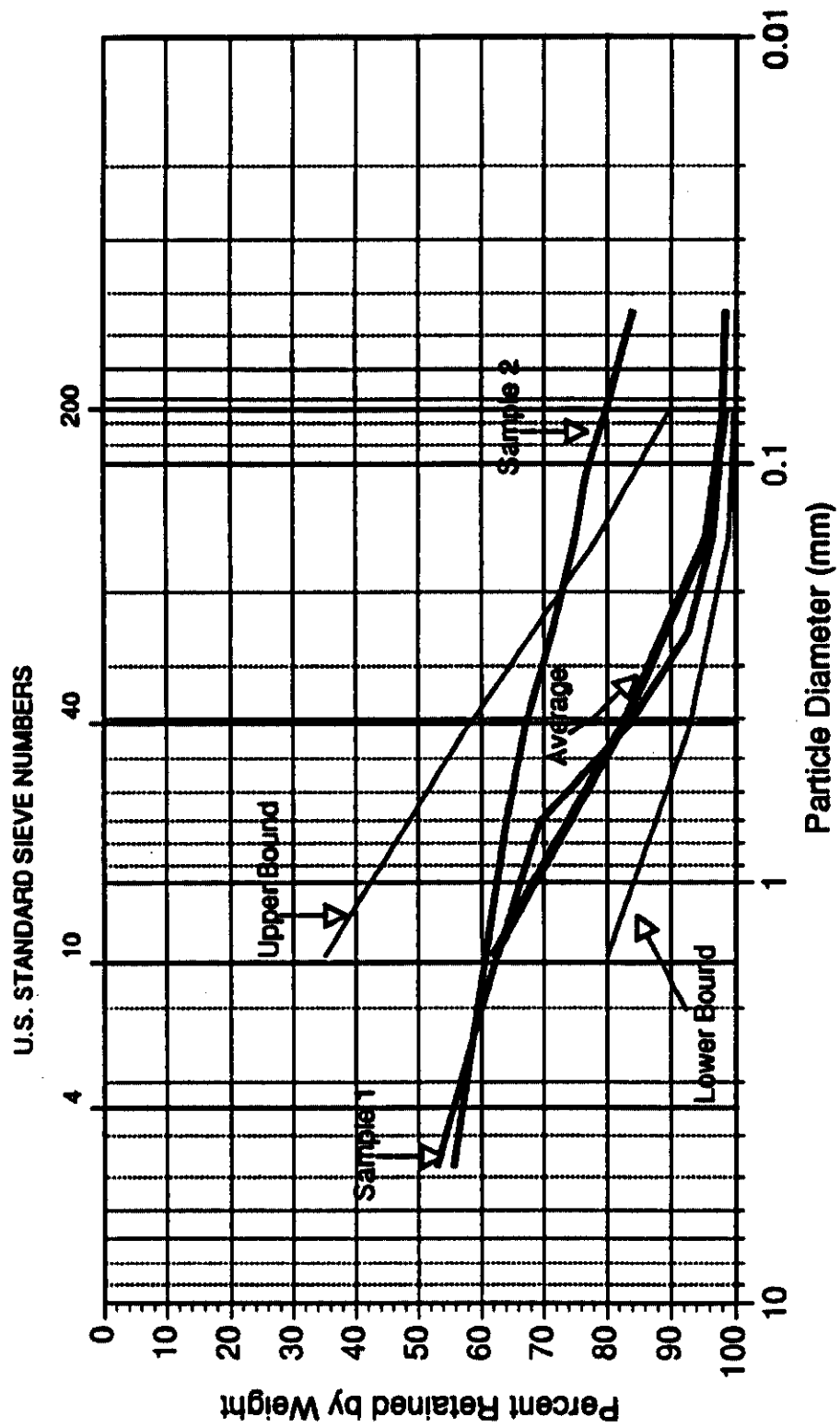


Fig. 2-3. Sample particle size comparison

destroyed by heating to 400°C leaving a dark residue. No further work was done with this heat treated material.

With Sample 1, a significant amount of radionuclide contamination in the smaller grain fractions (-4 mesh) was removed by physically separating the relatively highly radioactive fine fractions (-140 mesh) from the intermediate size fractions. These fine fractions account for less than 3% of the weight, but contain about 25% of the activity. Both flotation and sieving were successfully used to isolate the fines. With Sample 2, the radionuclides are distributed rather uniformly among the various -4 mesh fractions. Neither sieving nor flotation was effective in isolating or concentrating the radionuclides in a low weight percent fraction. With both methods, an excessive amount of the material processed (more than half) reported to the fines fraction.

Since it appears that the contamination remaining on the sediments after fines removal by sieving or flotation is coated on the sediment particle surface, abrading the surfaces followed by a second fines removal operation would be a successful method of physically removing the contamination. Attrition scrubbing (vigorous agitation of a concentrated slurry) is a common means of surface abrasion. With Sample 1, attrition scrubbing with an alkaline solution (sodium hydroxide or ammonium hydroxide) resulted in a somewhat better decontamination than hydrogen peroxide. An additional 50% reduction in contamination concentration was achieved. However, use of hydrogen peroxide is advantageous because it breaks down into water at a neutral pH, simplifying waste solution treatment. Attrition scrubbing with water was of little value. With successive attrition scrubs, the second yielded little additional contaminant reduction. With Sample 2, attrition scrubbing resulted in excessive fines production (4-8 times that of Sample 1). This was probably due to the soft organic material present being size reduced by the abrasive action of the attrition scrubber. Attrition scrubbing in a proprietary application of a halide solution yielded approximately the same contaminant reduction as ammonium hydroxide. The halide compound used in this process has the advantage in production-scale use because it can be regenerated and recycled on-site.

Another decontamination method used is the gentle mixing (stir washing) of the -4 mesh portion with a leaching and/or debonding solution followed by sieving and/or filtration to remove

debonded fines. In the tests reported here, stir washing followed attrition scrubbing. More than a dozen different stir wash conditions (reagents, time, and temperature) were tested. Five molar nitric acid at 70°C was found to be the most effective condition for decontaminating the sediments. Dilute nitric-acid, acetic acid with hydrogen peroxide, hydroxylamine with acetic acid, ethyl alcohol, and thiourea were all found to be ineffective. Neither isotopic dilution nor the addition of activated charcoal improved decontamination of the sediments by stir washing. The goal residual Cs-137 concentration of 690 pCi/g was attained with Sample 1 sediments using the 5 M nitric acid stir wash, but not with any of the other reagents tested. Fig. 2-4 summarizes the two successful integrated treatment tests with Sample 1 sediments. With Sample 2, none of the stir wash treatments, including 5 M nitric acid, attained the goal residual Cs-137 concentration. However, contaminant reductions in excess of 90% were attained. In a brief special test with a Sample 2 split, most of the organic material was destroyed by oxidation in a furnace prior to stir washing. This pretreatment operation enhanced the dissolution of Cs-137 and Co-60 in 5 M nitric acid, but not in an acetic acid-hydrogen peroxide mixture.

2.2 CONCLUSIONS

Testing conducted by NRT has shown that Warm Waste Pond sediments at the INEL has the potential to be remediated to acceptable residual radionuclide concentrations through a process combining the elements of physical and chemical separation methods. These operations included particle classification, froth flotation (optional), attrition scrubbing, and chemical leaching. In an exploratory test, the preoxidation of the organic material substantially improved the leachability of the Cs-137 and Co-60. Fine material routed to low level waste comprised 5-10% of the starting sample weight. Volumetrically this translates to 3-7% of original volume.

Bench scale tests with kilogram sample quantities have succeeded in cleaning 90% of the Warm Waste Pond sediments on a blended basis without the use of RCRA hazardous reagents or unacceptable secondary waste generation. Additional testing to support actual pilot plant design will be required. This testing should be design and process specific to enhance equipment selection and process definition for the selected design.

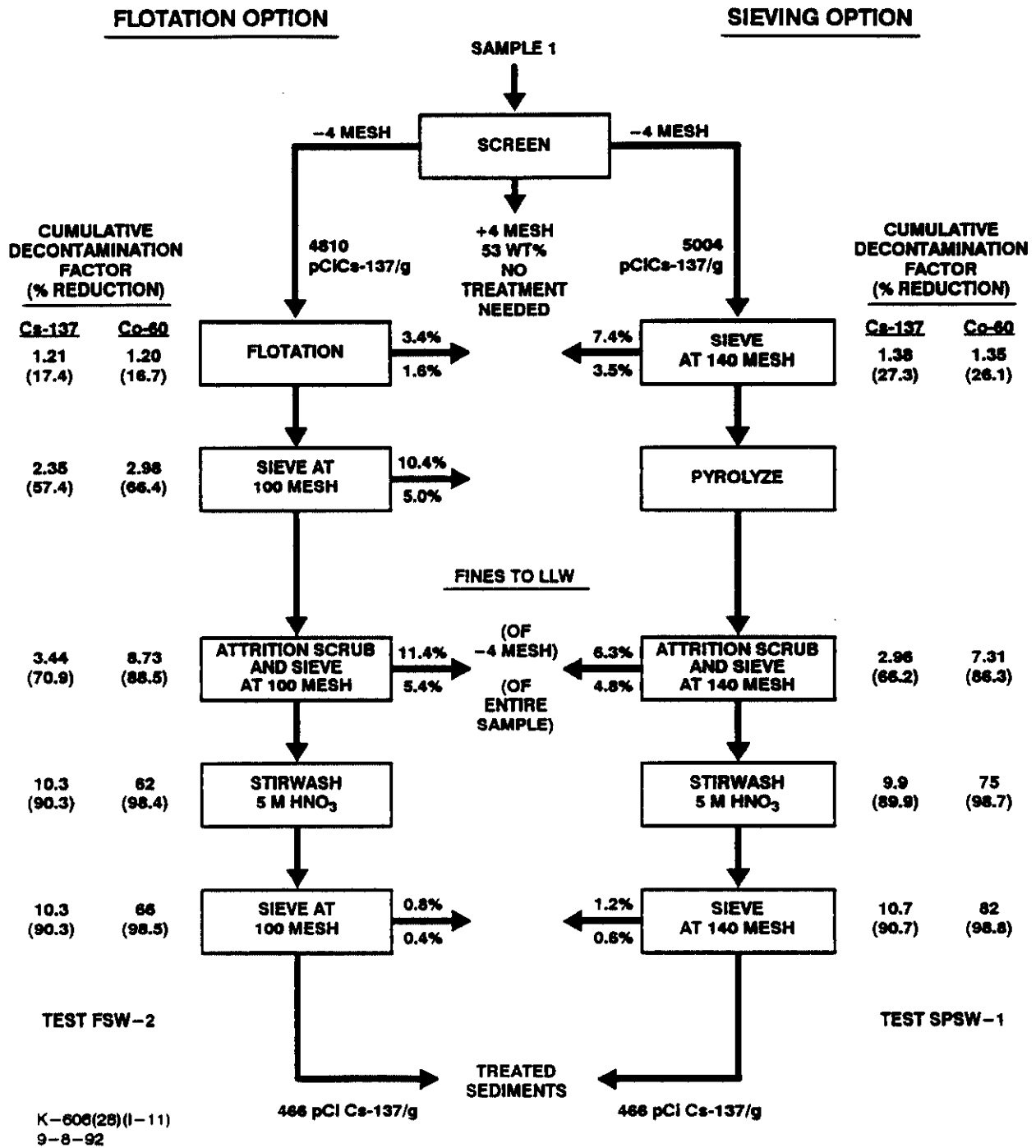


Fig. 2-4. WWP Sample 1 treatment options

Warm Waste Pond sediments high in organic matter content cause problems when introduced into the anticipated remediation process defined for low organic content sediments. Since the high organic matter sediments also contain high contaminant concentrations, effective WWP remediation requires that the high organic sediments be addressed. Oxidation of the organics as a preliminary process step show promise of rendering the high organic sediments compatible with demonstrated processes for low organic sediments. Additional testing, will be required to verify its effectiveness and its application to full pilot scale.

3.0 TEST RESULTS

3.1 EQUIPMENT AND PROCEDURES

All bench-scale test work on the treatment of the Warm Waste Pond sediments was conducted in the General Atomics Radiochemistry Facility in San Diego. Much of the equipment used in the testing consisted of normal chemical laboratory hardware. This includes sieves, balances, mixers, drying ovens, an ultrasonic bath, thermometers, etc. Specialized equipment used was a bench-scale WEMCO attrition scrubber (with a float cell attachment) and a Canberra S-100 gamma ray spectrometer. For stir wash contacts, four-liter beakers were used with agitation provided by a laboratory mixer with a mixer blade fashioned from stainless steel tubing. Tumble washing utilized 2-liter plastic bottles, which were rotated end over end, and a rock tumbler.

In the preliminary tests (Sample 1), the first rough sieving was done dry, but all subsequent sievings of the smaller mesh fractions were made using wet sieving techniques. Standard laboratory vacuum filters were used for separation of solids from liquids. Normally 540 filter paper was used to expedite filtration, but a few filtrates were subsequently passed through a 0.5 μm filter for further clarification. Solid fractions were dried prior to weighing.

Solutions and weights used were identified in laboratory notebooks. Samples submitted for gamma analysis were identified in the notebooks by weight and sample number for subsequent matching in the gamma spectrometer printout. To be accommodated in the spectrometer, the larger sized fractions (+1 in. and +½ in.) required size reduction.

3.2 FIRST SAMPLE TESTS

The various process steps and process quantities utilized in the exploratory (preliminary) testing with the first sample are shown in Figures 3-1, 3-2, and 3-3. Also included are the Cs-137 and Co-60 analytical results. No chromium analyses were performed in this testing stage. Test results were reviewed during the test program and determined the direction of subsequent process steps.

3.2.1 Preliminary Test Results

Sample Characterization. The 21.7-kg sample (Sample 1) of the Warm Waste Pond sediments was sieved into 13 size fractions. Each fraction was weighed and analyzed for Cs-137 and Co-60. Tables 3-1A and 3-1B contain a summary of the characterization results. Calculation details are contained in Ref. 5.

The results indicate a direct relationship between sediment grain size and concentrations of Cs-137 and Co-60. As the grain size decreases, the Cs-137 and Co-60 concentrations increase. Additionally, the ratio of both radionuclides remains roughly the same in all fractions. This suggests that Cs-137 and Co-60 concentrations are related to the surface area of a particular fraction. From the cumulative average Cs-137 and Co-60 concentrations listed in Table 3-1B, it appears that the large sediment material, constituting 50 weight percent or more of the total, can be screened out and would not require further processing to meet the remediated sediment goal of 690 pCi Cs-137/g (Ref. 2). The sizeable remaining sediment fraction, however, will require further treatment.

Based on the estimated Cs-137 to Co-60 content of the WWP sediments (Ref. 1), the Cs-137 to Co-60 radioactivity ratio is 3.33. The sample average ratio of 3.48 compares favorably with this estimate. Some ratio variation, however, exists among the several size functions. The large fractions (+12 mesh) and the fines (-325 mesh) have higher than average Cs-137 to Co-60 ratios (up to a ratio of 5.3).

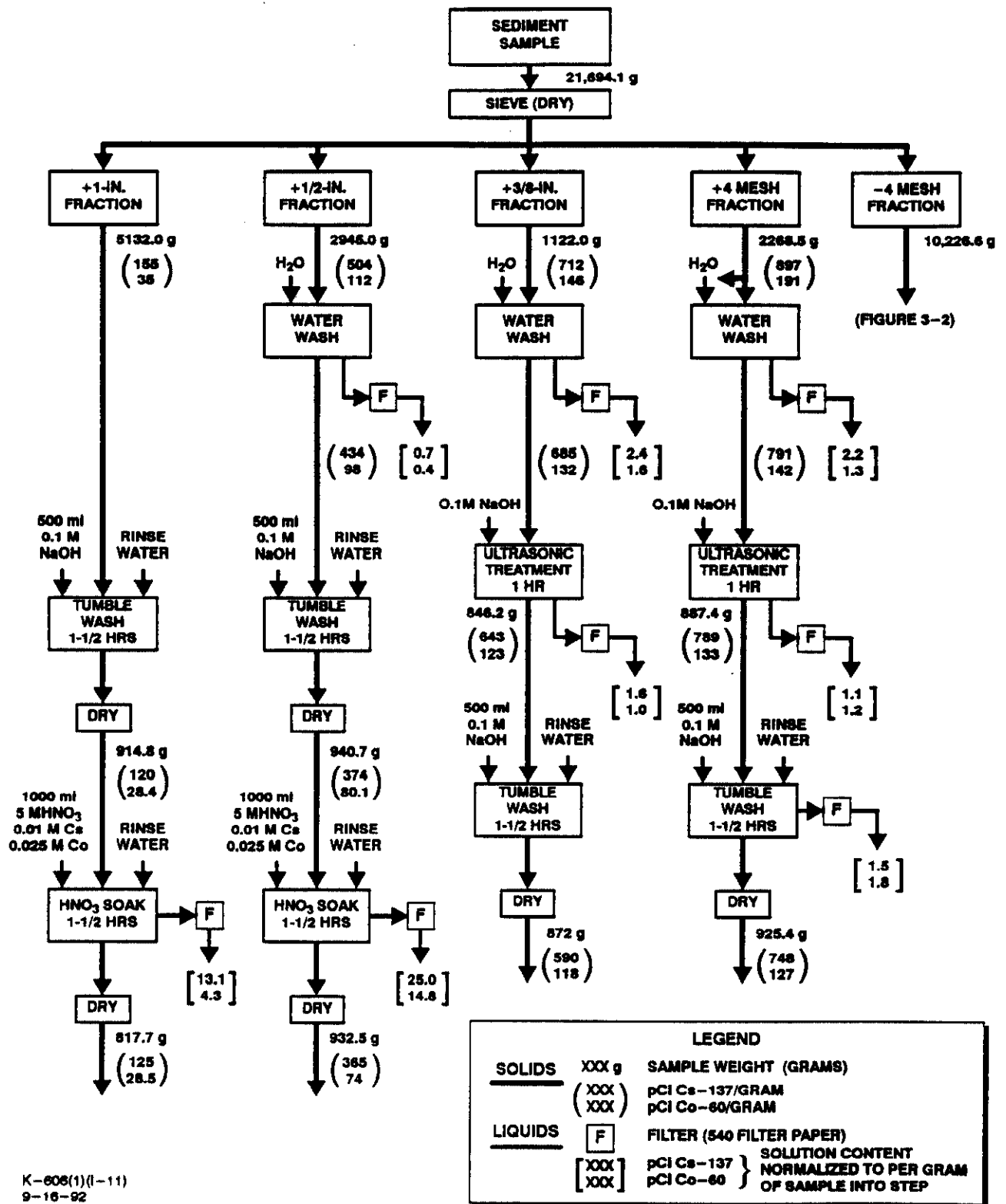


Fig. 3-1. Warm waste pond sediment treatment preliminary tests — coarse sieving and coarse fraction treatment

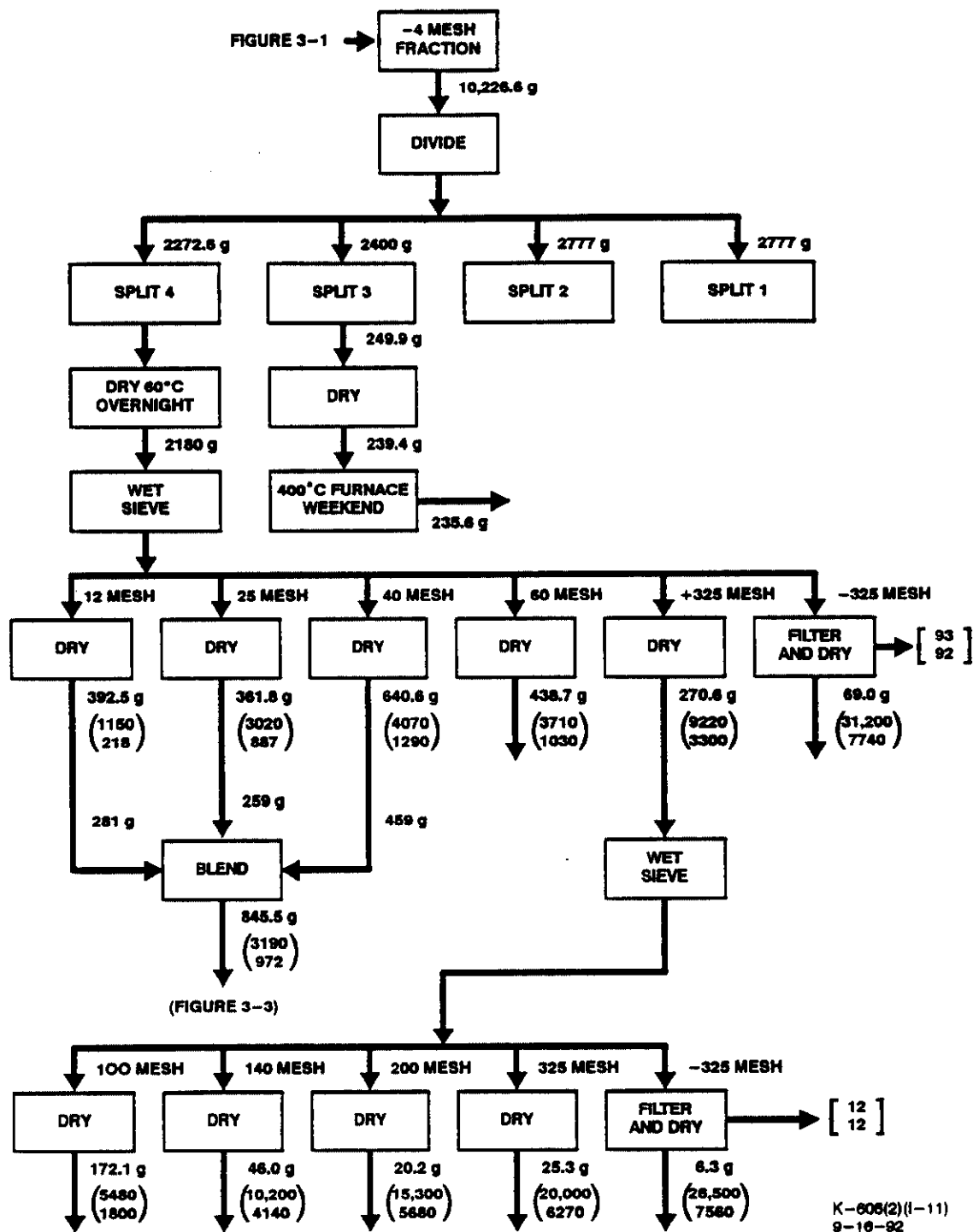
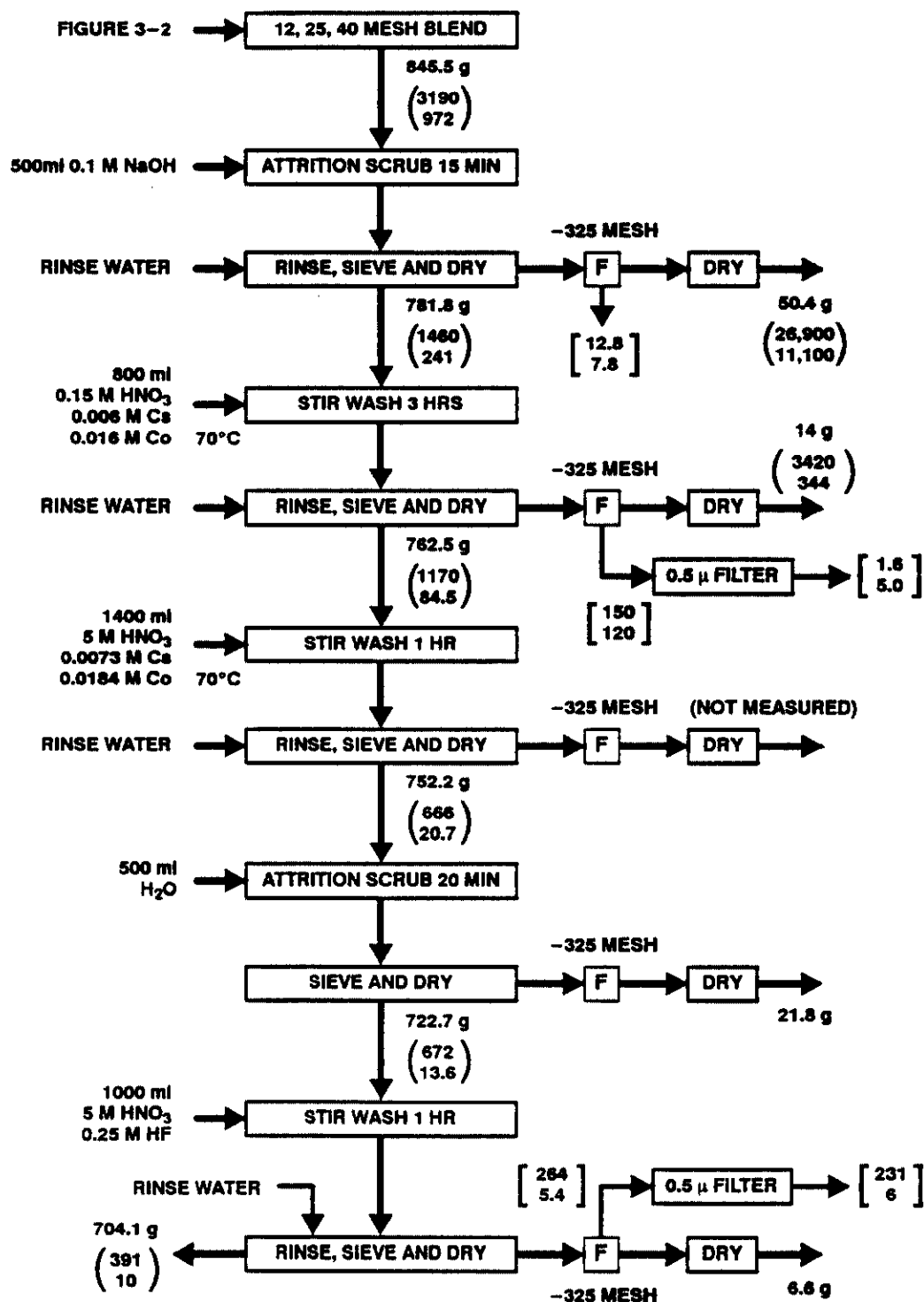


Fig. 3-2. Warm waste pond sediment treatment preliminary tests — fine sieving



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Fig. 3-3. Warm waste pond sediment treatment preliminary tests — mid fraction treatment

Table 3-1A
First Sample Characterization Results - Large to Small

Retained Fraction	Weight, g		Analysis, pCi/g		Cumulative Average Concentration, pCi/g		Cumulative Percentages		
	Fraction	Cumulative	Cs-137	Co-60	Cs-137	Co-60	Weight	Cs-137	Co-60
1 inch	5132.0	5132.0	155	35	155	35	23.69	1.49	1.17
½ inch	2945.0	8077.0	504	112	282	63	37.29	4.25	3.32
¾ inch	1122.0	9199.0	712	146	334	73	42.47	5.73	4.38
4 mesh	2268.5	11467.5	897	191	445	97	52.95	9.53	7.20
12 mesh	1841.2	13308.7	1150	218	543	113	61.45	13.49	9.81
25 mesh	1697.2	15005.9	3020	887	823	201	69.28	23.07	19.64
40 mesh	3005.1	18011.0	4070	1290	1365	383	83.16	45.91	44.88
60 mesh	2057.9	20068.9	3710	1030	1604	449	92.66	60.15	58.67
100 mesh	807.3	20876.2	5480	1800	1753	502	96.39	68.37	68.11
140 mesh	215.8	21092.0	10200	4140	1840	539	97.38	72.38	73.90
200 mesh	94.8	21186.8	15300	5680	1902	562	97.82	75.28	77.41
325 mesh	118.7	21305.5	20000	6070	2002	593	98.37	79.67	82.22
-325 mesh	353.3	21658.8	30800	7740	2470	710	100.00	100.00	100.00

Table 3-1B
First Sample Characterization Results - Small to Large

Retained Fraction	Cumulative Percentages									
	Weight, g		Cumulative Average Concentration, pCi/g		Entire Sample			-4 Mesh		
	Fraction	Cumulative	Cs-137	Co-60	Weight	Cs-137	Co-60	Weight	Cs-137	Co-60
-325	353.3	353.3	30800	7730	1.63	20.32	17.76	3.47	22.47	19.14
325	118.7	472.0	28070	7360	2.18	24.75	22.60	4.63	27.36	24.35
200	94.8	566.8	25940	7080	2.62	27.46	26.10	5.56	30.35	28.12
140	215.8	782.6	21600	6270	3.61	31.57	31.91	7.68	34.90	34.38
100	807.3	1589.9	13410	4000	7.34	39.83	41.35	15.60	44.02	44.55
60	2057.9	3647.8	7940	2320	16.84	54.08	55.14	35.79	59.78	59.41
40	3005.1	6652.9	6190	1860	30.72	76.93	80.42	65.28	85.03	86.64
25	1697.2	8350.1	5550	1660	38.55	86.51	90.24	81.93	95.62	97.22
12	1841.2	10191.3	4750	1400	47.05	90.47	92.82	100.00	100.00	100.00
4	2268.5	12459.8	4050	1180	57.53	94.26	95.64			
3/8 inch	1122.0	13581.8	3770	1090	62.71	95.76	96.68			
1/2 inch	2945.0	16526.8	3190	920	76.31	98.52	98.83			
1 inch	5132.0	21658.8	2470	710	100.00	100.00	100.00			

An estimate of the first sample organic material content was made by noting the mass change resulting from heating a dried aliquot of the -4 mesh portion (split 3) in a 400°C furnace for approximately 65 hours. The weight loss was 1.59%. On this basis, the estimated organic content for the entire sample is 0.75%.

Large-Sized Material Treatment. Although the larger sediment material fraction could forego further treatment, under conditions of the ROD (Ref. 2), exploratory tests were made on their decontamination by various solutions. Figure 3-1 illustrates the tests undertaken, along with the analytical results. The tests included a simple water wash, contact with 0.1 M NaOH in an ultrasonic bath, tumble washing with 0.1 M NaOH and a nitric acid soak. Table 3-2 summarizes the decontamination factors and contaminant reduction percentages obtained. Calculation details are contained in reference 5.

The results indicated a significant amount of Cs-137 and Co-60 can be removed by a simple water rinse. Tumble washing appeared to be effective for the 1 inch and ½ inch fractions, but provided little benefit for the small grain fractions. It should be noted that the 1 inch fraction was not water washed prior to tumbling, as were the other fractions. This, to some extent, accounted for its higher tumble wash contaminant reduction factors.

Ultrasonic treatment resulted in very little Cs-137 or Co-60 removal. A nitric acid soak appeared to be more effective for Co removal than Cs. However, significant dissolution of the sediment material can occur, introducing a waste solution treatment concern. More than 10% of the 1 inch fraction dissolved during its HNO₃ soak. During this work, significant bubbling was noted from one rock. This is indicative of the sludge generation concern resulting from the treatment of large sediment quantities with hot nitric acid.

Of particular interest was how the removed Cs-137 and Co-60 is distributed between the spent treatment solutions and the -325 mesh fines removed from the waste solution by filtration. Table 3-3 lists this distribution. Typically more than 90% of the removed Cs-137 and Co-60 remained on the solids. The apparently low Cs-137 and Co-60 content in the 4 mesh ultrasonic treatment fines was likely due to measurement uncertainties. The Cs-137 and Co-60 content in

Table 3-2
First Sample Large Size Material Treatment Results

Fraction	Decontamination Factor ⁽¹⁾ (% Contaminant Reduction) ⁽⁴⁾							
	Water Wash		Ultrasonic Treatment ⁽²⁾		Tumble Wash ⁽²⁾		5M HNO ₃ Soak ⁽³⁾	
	Cs-137	Co-60	Cs-137	Co-60	Cs-137	Co-60	Cs-137	Co-60
1 inch	--	--	--	--	1.29 (22.6)	1.23 (18.9)	1.00 ⁽⁵⁾ (0)	1.00 ⁽⁵⁾ (0)
½ inch	1.16 (13.9)	1.14 (12.5)	--	--	1.16 (13.8)	1.22 (18.3)	1.02 (2.4)	1.08 (7.6)
¾ inch	1.04 (3.8)	1.11 (9.6)	1.07 (6.1)	1.07 (6.8)	1.09 (8.2)	1.04 (4.1)	--	--
4 mesh	1.13 (11.8)	1.35 (25.7)	1.003 (0.3)	1.07 (6.3)	1.05 (5.2)	1.05 (4.5)	--	--

⁽¹⁾ Activity in feed divided by activity in product

⁽²⁾ In 0.1 M NaOH

⁽³⁾ Also contained 0.01 M CsNO₃ and 0.025 M Co (NO₃)₂

⁽⁴⁾ $\frac{(\text{Feed concentration} - \text{product concentration})}{\text{feed concentration}} \times 100$

⁽⁵⁾ Product sample had a higher value than feed - a DF of 1.00 was assigned

Table 3-3
Large Sized Material Treatment Wastes
Distribution of Activity Between Solution and Fines

Fraction	Fraction of Removed Cs-137 and Co-60 in Fines ⁽¹⁾					
	Water Wash		Ultrasonic Treatment		Tumble Wash	
	Cs-137	Co-60	Cs-137	Co-60	Cs-137	Co-60
1 inch	--	--	--	--	--	--
½ inch	99	97	--	--	--	--
¾ inch	91	89	96	89	--	--
4 mesh	97	97	45 ⁽²⁾	9 ⁽²⁾	97	80

⁽¹⁾ Component in treatment fines (-325 mesh) divided by total component removed

⁽²⁾ Calculation includes the difference between two large numbers close in value resulting in high uncertainty

the fines was calculated using the difference between the input and output values. Since the contaminant reduction factor was low, the uncertainty in the difference was magnified.

The results suggest wet screening should be used as an aid in separating the relatively radioactive fines from the relatively nonradioactive rocks.

Intermediate-Sized Material Treatment. A blend of the 12, 25, and 40 mesh fraction from the characterization effort (Figure 3-2) was chemically and physically treated for removal of contamination. Figure 3-3 presents the process steps used, the process conditions, and analytical results. Table 3-4 contains a summary of the treatment results.

Because of sample quantity limitations, the process steps were done sequentially with the same sediment sample fraction. Performing the later stage process steps with previously untreated samples would likely yield different results.

One significant finding was that essentially all of the removed activity existed in the solid fines (-325 mesh) fraction rather than in solution. This finding was in agreement with the results from the large fraction treatment. Only in the treatment step using hydrofluoric acid did a significant fraction of the Cs-137 and Co-60 dissolve. In general, Co-60 was more readily removed than Cs-137. Attrition scrubbing in dilute sodium hydroxide resulted in significant decontamination, but at the expense of generating a significant quantity of -325 mesh fines (6% of the feed.) Since the activity was in the fine material, it was necessary to remove the fines to achieve significant contaminant removal. Attrition scrubbing with water was ineffective in reducing the concentration of Cs-137 in the product. The total quantity of Cs-137 in the product was reduced only because of fines formation and their subsequent removal by sieving.

Material balances were determined around process steps where a sufficient number of measurements were performed. Not all of the Cs-137 and Co-60 could be accounted for (typically 10%). This could be due to the inability to completely recover the -325 fines fraction from the filter paper. Since the fines fraction contained the highest concentration of Cs-137 and Co-60, a small recovery deficit would have a relatively large impact on Cs-137 and Co-60 balance.

Table 3-4
12, 25, and 40 Mesh Blend Treatment Summary

Sequential Process Step	Fraction Dissolved ⁽¹⁾			Fraction In Fines ⁽²⁾			Fines/Solution ⁽³⁾		Decontamination Factor ⁽⁴⁾		% Contaminant Reduction ⁽⁵⁾	
	Wt	Cs-137	Co-60	Wt	Cs-137	Co-60	Cs-137	Co-60	Cs-137	Co-60	Cs-137	Co-60
0.1 M NaOH Attrition Scrub	0.016	0.0040	0.0080	0.060	0.50	0.68	125	85	2.18	4.03	54.2	75.2
Dilute HNO ₃ Wash	0.0068	0.0011	0.021	0.018	0.144	0.502	130	24	1.25	2.85	19.9	64.9
5 M HNO ₃ Wash	--	--	--	--	--	--	--	--	1.76	4.08	43.1	75.5
Water Attrition Scrub	--	--	--	0.029	--	--	--	--	1.00 ⁽⁶⁾	1.58	0.0	34.3
5 M HNO ₃ , 0.25 M, HF Wash	0.0091	0.344	0.442	--	--	--	--	--	1.72	1.36	41.8	26.5

⁽¹⁾ Quantity determined to be in filtered waste solution divided by quantity in process step feed

⁽²⁾ Quantity determined to be in the -325 fraction fines divided by quantity in process step feed

⁽³⁾ Quantity in -325 fines fraction divided by quantity in waste solution

⁽⁴⁾ Feed activity divided by product activity

⁽⁵⁾
$$\frac{(\text{Feed concentration} - \text{product concentration})}{\text{feed concentration}} \times 100$$

⁽⁶⁾ Product sample had a higher value than feed - a DF of 1.00 was assigned

3.2.2 Preliminary Flotation Tests

The sediment characterization and exploratory testing described above indicated the bulk of the Cs-137 and Co-60 contamination was associated with the fine grain fractions. In the mining industry, the most common method of separating fines from other material is by flotation. Flotation is particularly applicable where a large quantity of material, such as the Warm Waste Pond sediments, is to be processed.

For bench-scale testing, simple attachments to the attrition scrubber used in the earlier tests permitted its operation as a flotation cell. An essential consideration in the preliminary bench-scale tests was the limited quantity of Warm Waste Pond sediment samples and the minimum quantity required per test (about 150 grams with 750 grams or more preferred).

Equipment and procedural shake-down tests were made using local (San Diego) soil spiked with organic material (dried steer manure). These tests indicated a need for a cover on the froth bath to limit potential contamination spread. A suitable cover was fabricated and utilized in the subsequent testing.

Initial tests with Warm Waste Pond sediments focused on determining which flotation reagents yield the best sediment decontamination. Since the sediments contained organics (Ref. 1) and the organics were likely to have high concentrations of the contaminants, the choice of flotation reagents included those that are specific for organic removal.

Two types of reagents were used in the flotation tests. The first, frothers, helped form a stable froth of air bubbles upon which the desired sediment fractions float to the surface of the agitated and aerated slurry. The two frothers used were:

1. Pine Oil
2. MIBC/F65

The pine oil used was HERCO® Pine Oil (terpineol) produced by Hercules Incorporated, Wilmington, Delaware. Other uses include household disinfectants and cleaners. MIBC/F65

consists of three parts methyl-isobutyl carbinol (methyldamyl alcohol) to one part F65 (Aerofroth® 65 Frother). The MIBC used was manufactured by EM Science, Gibbstown, New Jersey. F65 is a polypropylene glycol manufactured by American Cyanamid Co, Wayne, New Jersey.

The other type of reagent used is a collector (promoter). This reagent type provides the sediment fractions to be floated with a water repellent, air-avid coating that attaches to air bubbles. The collectors were added about five minutes prior to frother addition to condition the sediments for flotation. The three conditioners used were:

1. Emulsified high-density mineral oil
2. A208
3. Armac T

The mineral oil was supplied by Eastman Kodak Company, Rochester, New York. The emulsion used consisted of 20 parts water, 2 parts mineral oil, and 0.2 parts SCS emulsifying agent. A208 (Aerofroth® 208 Promotor) is a phosphorodithioate salt mixture supplied by American Cyanamid Co., Wayne, New Jersey. It has been used for many years as a flotation agent. Armac® T is a tallow amine acetate mixture manufactured by AKZO Chemicals, Inc., Chicago, Illinois. It is a widely used flotation agent for quartz and silicates. It was added as a 1 wt% aqueous solution.

Reagent concentrations commonly used in mineral dressing are 0.1 to 0.5 pounds per ton of ore processed. Flotation tests of Warm Waste Pond sediments used reagent concentrations in this range. A float cell attachment to a bench-scale WEMCO attrition scrubber was used for the tests.

In operation, the frother was added about five minutes after the conditioner addition. The air inlet valve was then opened and the froth manually skimmed from the bath with a spatula and collected in a tray. Water was added as needed to maintain level. A test was considered to be complete when a scum of sediments was no longer apparent on the froth. In each of the preliminary tests, multiple reagent additions were made sequentially. The test conditions and results of these preliminary tests are contained in Figures 3-4 through 3-8. The feeds used for

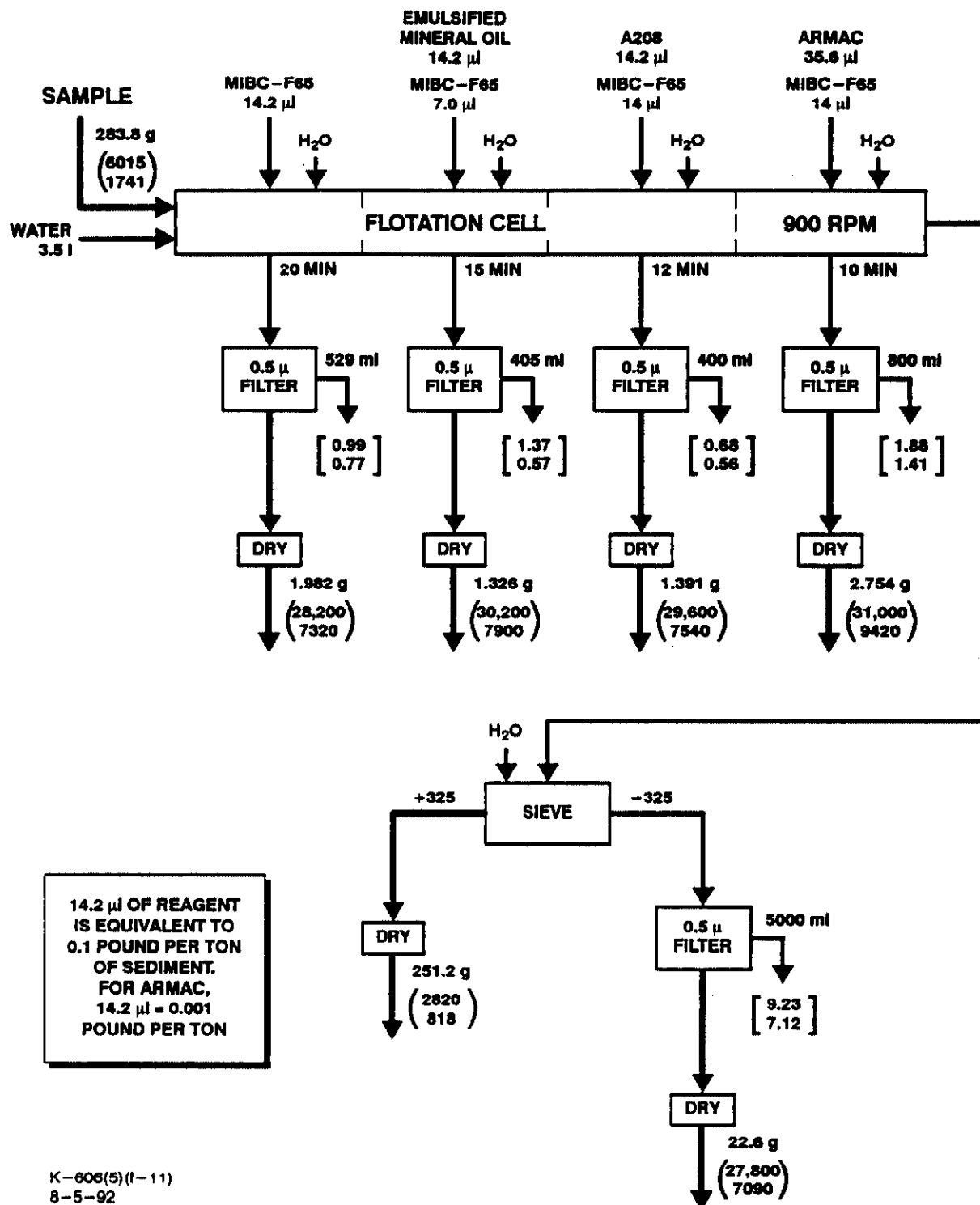


Fig. 3-4. Preliminary flotation test — Series A

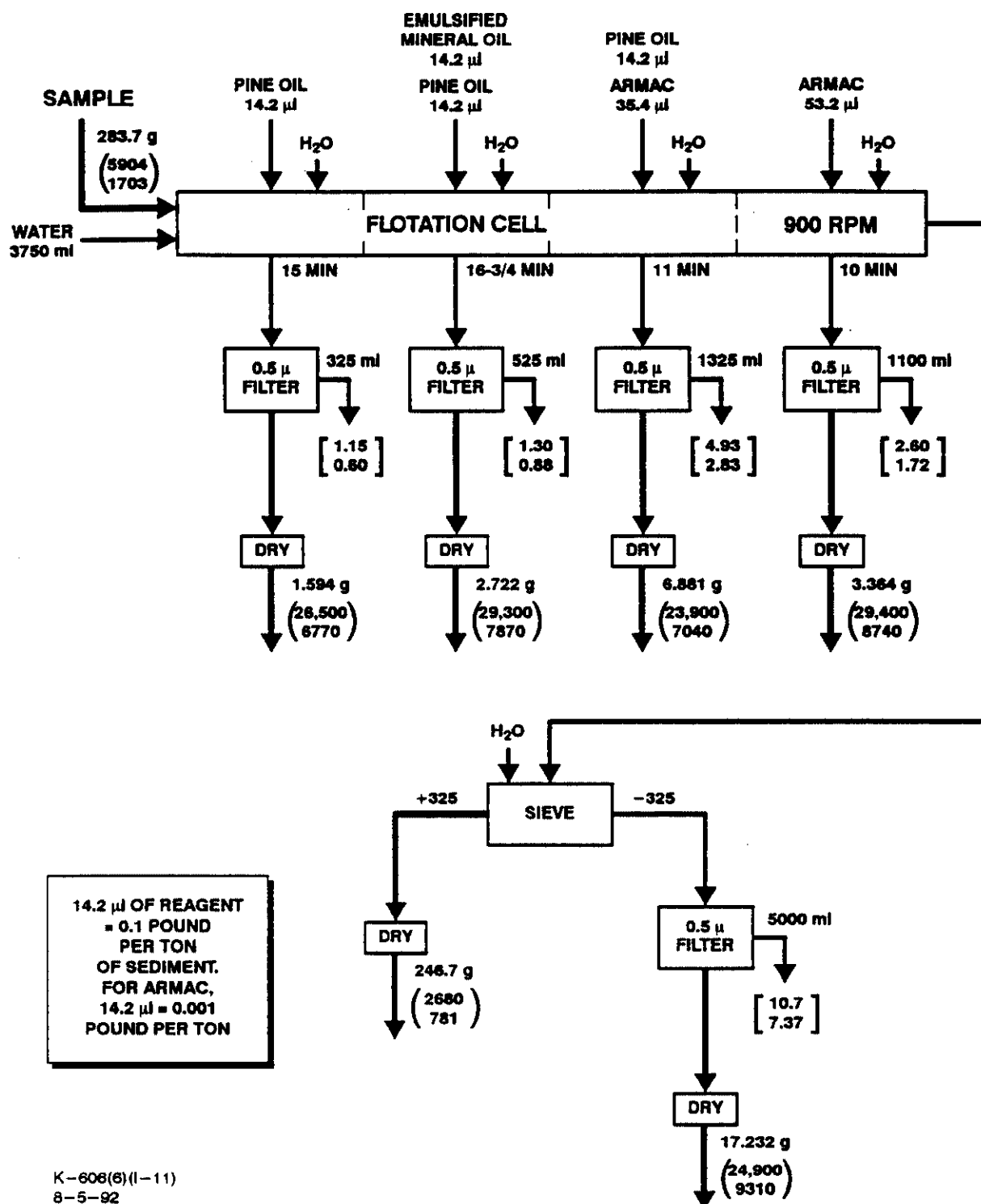
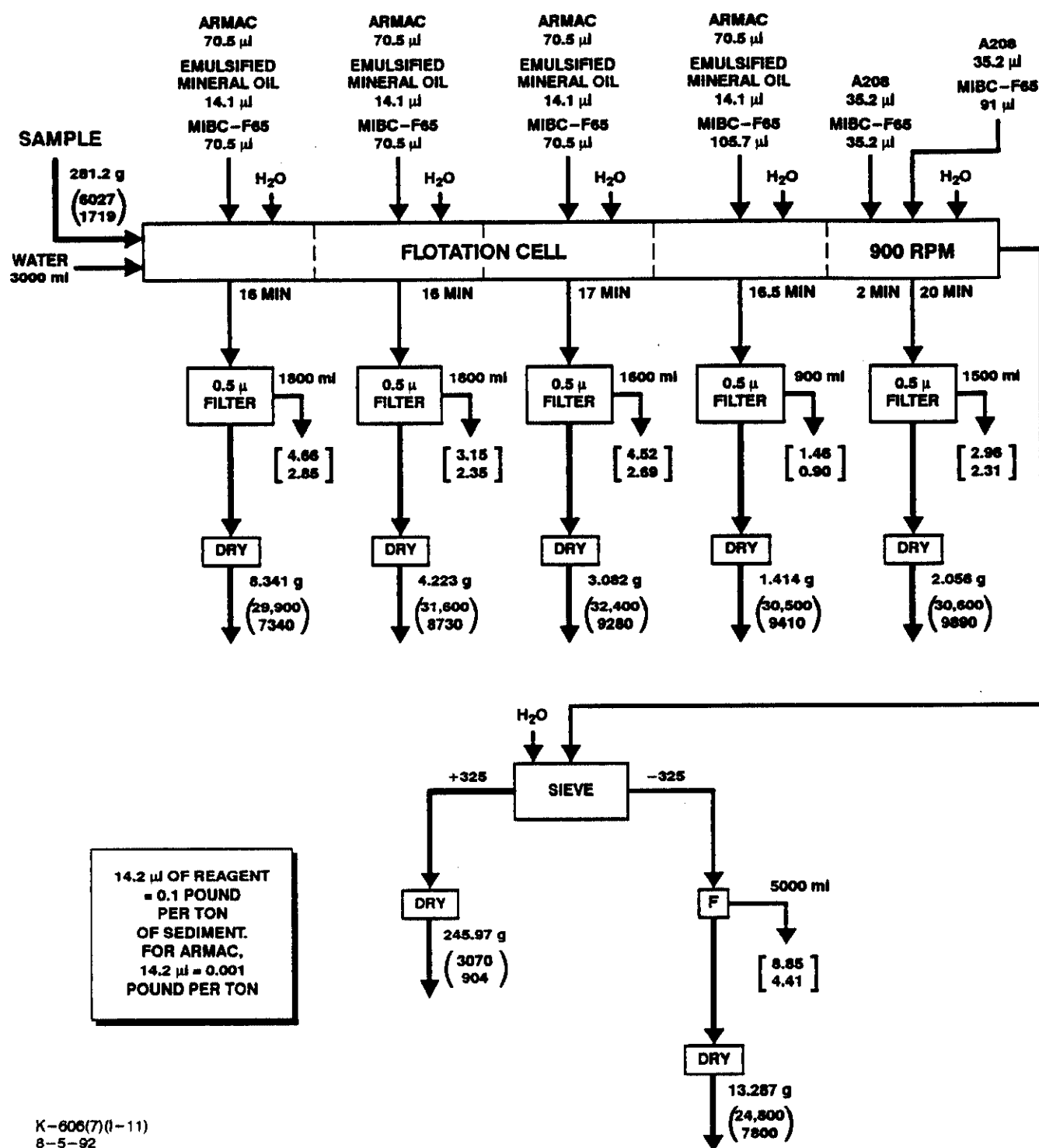
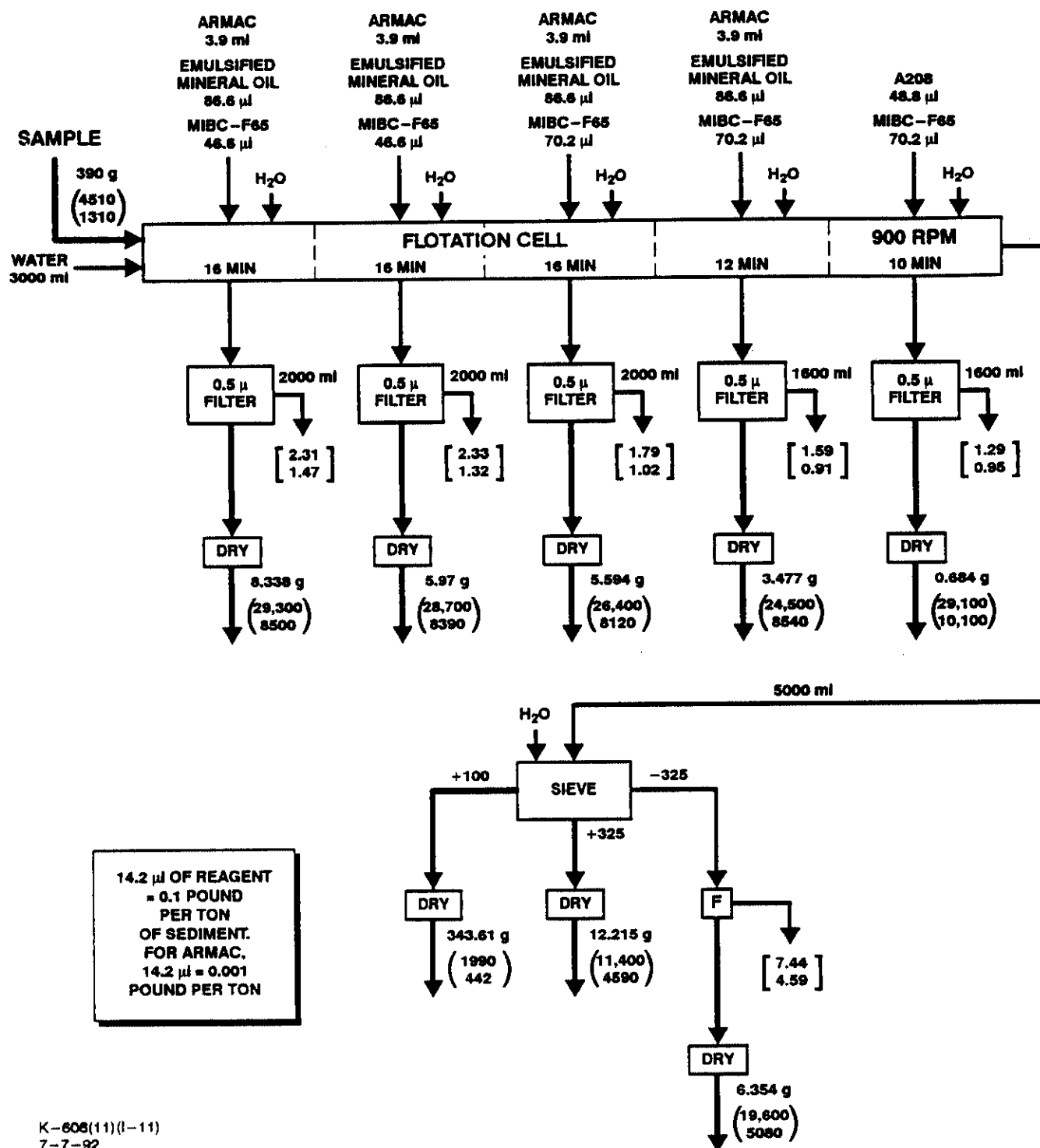


Fig. 3-5. Preliminary flotation test — Series B



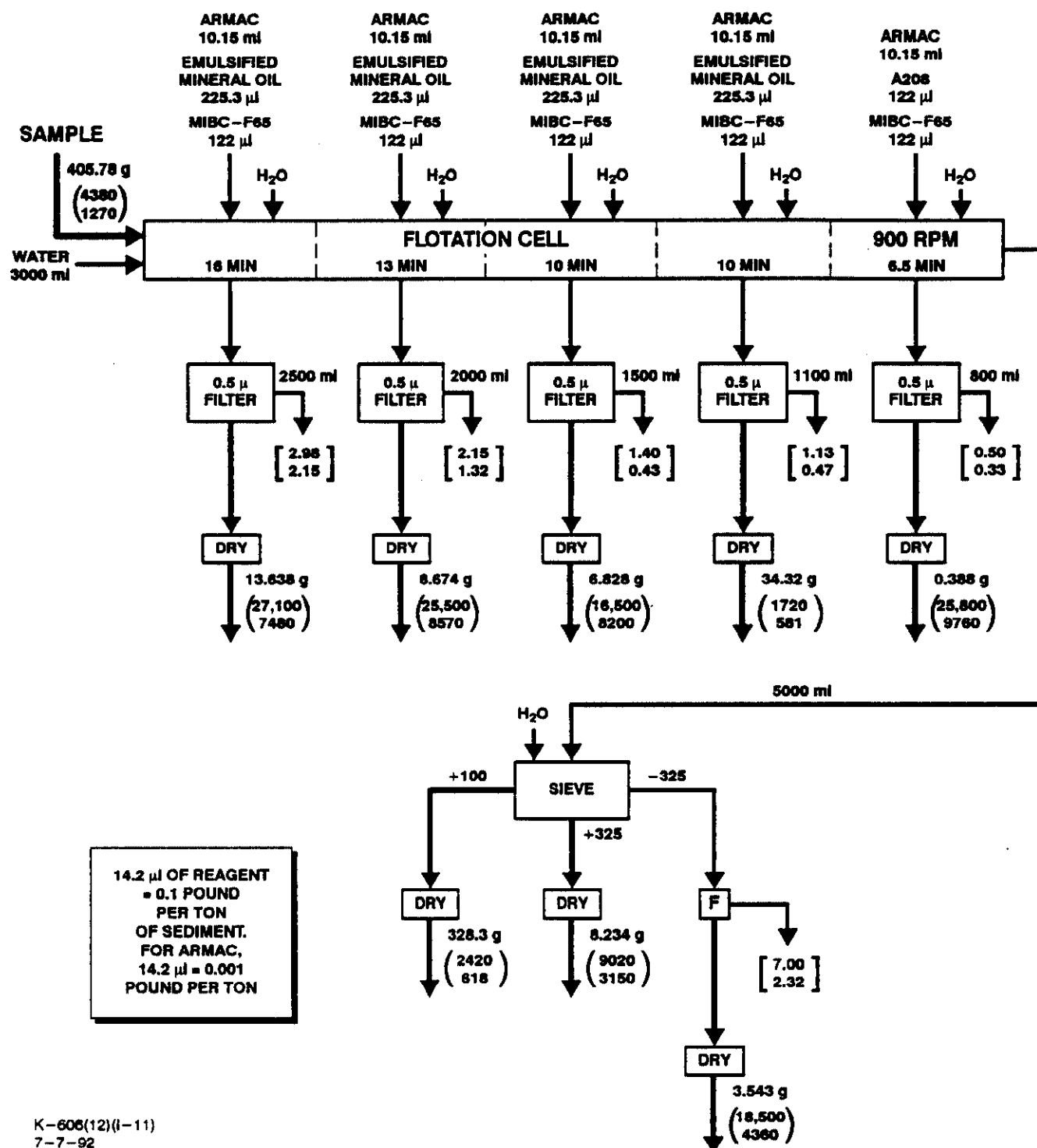
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Fig. 3-6. Preliminary flotation test — Series C



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Fig. 3-7. Preliminary flotation test — Series D



K-606(12)(I-11)
 7-7-92

Fig. 3-8. Preliminary flotation test — Series E

test series A, B, and C were prepared by recombining the various -4 mesh fractions resulting from the sample characterization effort (Fig. 3-2) in approximately the same proportions as in the initial sample, then adding additional -325 mesh fraction to raise the initial contaminant levels. This increased the -325 mesh fraction from 3.67 wt% to 8.42 wt%. For flotation test series D and E, the feed was prepared by combining, mixing, and then splitting the +325 and -325 mesh tails from flotation test series A, B, and C.

The concentrations of Cs-137 and Co-60 in float fractions are typical of those in the sediment fines. This shows that flotation can be used as a means of removing the fines from the bulk of the sediments. Table 3-5 contains the details of the various flotation tests made with Sample 1 including the flotation steps of the integrated tests.

The results indicate a reagent combination of emulsified mineral oil and MIBC-F65 conditioners with the Armac tallow amine frothers is the most effective combination for fines removal. By flotation, 40 to 45% of the contaminants can be concentrated into 6 to 7% of the flotation feed (3.5 to 4% of the original sediment weight).

3.2.3 Preliminary Attrition Scrub Tests

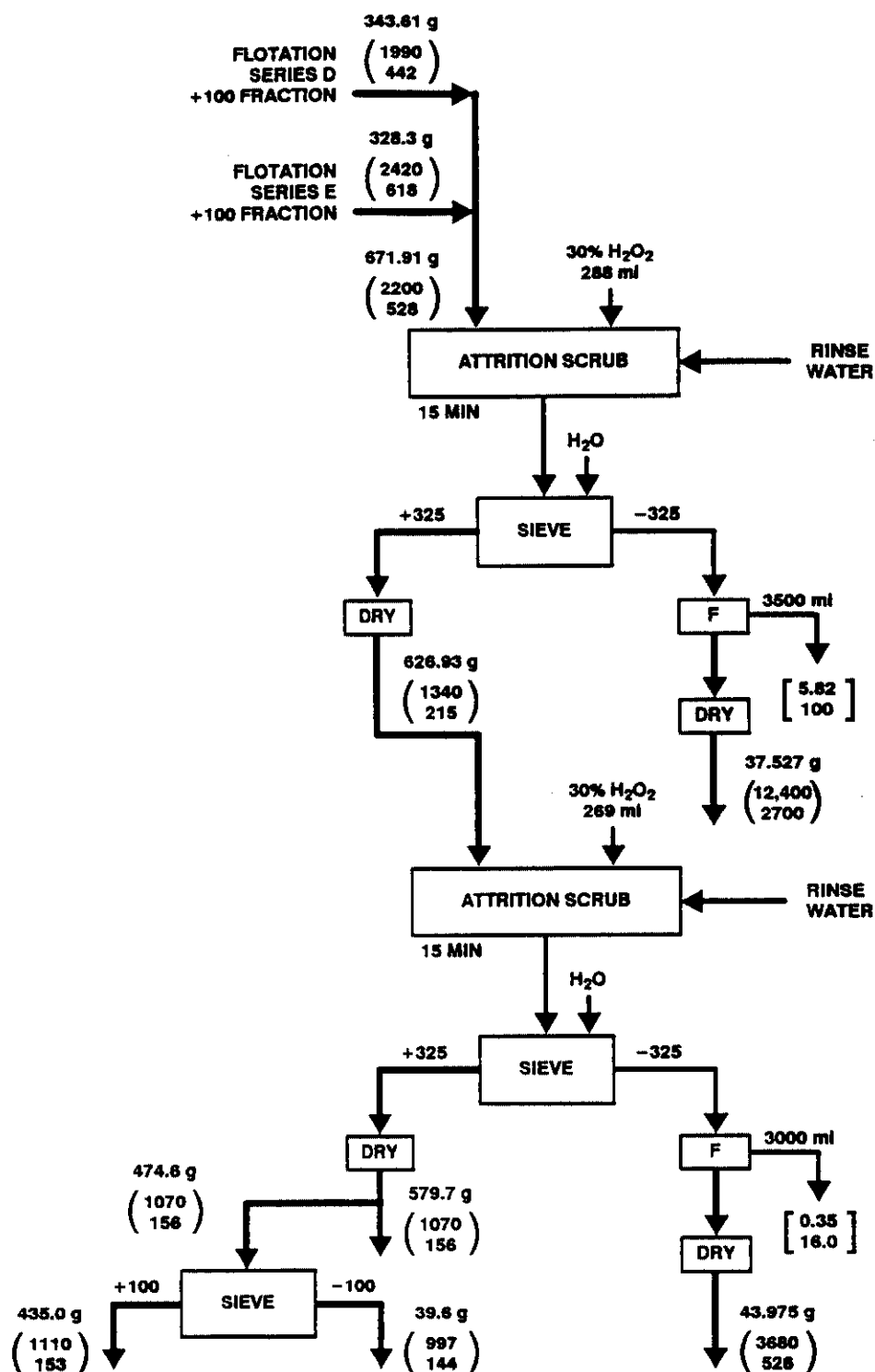
The +100 mesh fractions from flotation test series D and E were combined and processed through two stages of attrition scrubbing with 30% hydrogen peroxide at a pulp density of 70%. The attrition scrub products were sieved to remove the -325 mesh fines generated by the scrubbing. Figure 3-9 shows the test conditions and stream analyses. During the first attrition scrub, excessive foaming caused the loss of some of the material (approximately 1% by weight, but 10 to 15% of the contaminants). Table 3-6 contains a summary of the hydrogen peroxide attrition scrub test results. The contaminant removal factors obtained in the first attrition scrub stage were more than a factor of two higher than those from the second stage. The fraction of the Co-60 that dissolved in the hydrogen peroxide scrub solution was significant (0.22 in the first scrub) and much higher than the Cs-137 fraction dissolved (<0.01). The results indicate that there is little to be gained by successive attrition scrubs with the same reagent. The +325 mesh product from the second stage scrub was further sieved into a +100 mesh fraction and a -100 mesh fraction. Unexpectedly, the -100 mesh fraction had slightly

TABLE 3-5
WARM WASTE POND PRELIMINARY FLOTATION TESTS

Series	Flotation Reagent	Stage	Frother Concent. (lbs/ton solids)	Reagent Concent. (lbs/ton solids)	Flotation Time (min)	Weight of -4 Mesh Sample, g	Weight of Fines (-325) in -4 Mesh Sample		Weight of Flot. Conc., g	Wt% Flot. Conc. of -4 Mesh Feed	pCi/g			% Recovered Activity in Flotation Concentrate ⁽¹⁾		Concentration Factor ⁽²⁾	
							g	%			In Concentrate		In Feed	% Recovered Activity in Flotation Concentrate ⁽¹⁾			
											Cs-137	Co-60		Cs-137	Co-60	Cs-137	Co-60
							g	%			Cs-137	Co-60	Cs-137 Co-60 1741	Cs-137	Co-60	Cs-137	Co-60
A	MIBC-F65	1	0.100		20	283.8	24.4	8.60	1.982	0.70	28.200	7.320	6015 1741	3.58	3.37	4.7	4.2
A	Emulsified Mineral Oil/MIBC-F65	2	0.050	0.009	15				1.326	0.47	30.200	7.900		2.58	2.44	5.0	4.5
A	A208/MIBC-F65	3	0.100	0.100	10				1.391	0.49	29.600	7.540		2.64	2.44	4.9	4.3
A	Armec Tallow Amine Acetate Salt/MIBC-F65	4	0.100	0.0025	10				2.754	0.97	31.000	9.420		5.48	6.03	5.2	5.4
A	Totals		0.350	0.1115	55	283.8	24.4	8.60	7.453	2.63	29.850	8.240		14.24	14.28	5.0	4.7
B	Pine Oil	1	0.100		15	283.7	24.4	8.60	1.594	0.56	26.500	6.770	5904 1703	2.85	2.31	4.5	4.0
B	Emulsified Mineral Oil/Pine Oil	2	0.100	0.009	16.7				2.722	0.96	29.300	7.870		5.38	4.59	5.0	4.6
B	Armec Tallow Amine Salt/Pine Oil	3	0.100	0.0025	11				6.881	2.43	23.900	7.040		11.11	10.37	4.0	4.1
B	Armec Tallow Amine Salt	4	0.100	0.0038	10				3.364	1.19	29.400	8.740		6.62	6.30	5.0	5.1
B	Totals		0.400	0.0153	52.7	283.7	24.4	8.60	14.561	5.13	26.400	7.556		25.97	23.67	4.6	4.4
C	Armec Amine/Emulsified Mineral Oil/MIBC-F65	1	0.500	0.509	16	281.2	24.3	8.64	8.341	2.97	29.900	7.340	6027 1719	14.84	12.48	5.0	4.3
C	Armec Amine/Mineral Oil/MIBC-F65	2	0.500	0.059	16				4.223	1.50	31.600	8.730		7.94	7.51	5.2	5.1
C	Armec Amine/Mineral Oil/MIBC-F65	3	0.500	0.059	17				3.082	1.10	32.400	9.280		5.94	5.63	5.4	5.4
C	Armec Amine/Mineral Oil/MIBC-F65	4	0.750	0.059	16.5				1.414	0.50	30.500	9.410		2.57	2.71	5.1	5.5
C	A208/MIBC-F65	5	1.250	0.500	22				2.058	0.73	30.800	9.860		3.74	4.14	5.1	5.8
C	Totals		3.500	0.736	87.5	281.2	24.3	8.64	19.116	6.80	30.800	6.390		35.03	32.67	5.1	4.9
D	Armec Amine/Emulsified Mineral Oil/MIBC-F65	1	0.240	0.240	16	390.0	24.42	6.26	6.338	2.14	29.300	6.500	4510 1310	15.06	15.85	6.5	6.5
D	Armec Amine/Mineral Oil/MIBC-F65	2	0.240	0.240	16				5.970	1.53	28.700	8.390		10.56	11.20	6.4	6.4
D	Armec Amine/Mineral Oil/MIBC-F65	3	0.360	0.240	10				5.594	1.43	26.400	6.120		9.10	10.16	5.9	6.2
D	Armec Amine/Mineral Oil/MIBC-F65	4	0.360	0.240	12				3.477	0.89	24.500	6.540		5.25	6.64	5.4	6.5
D	A208/MIBC-F65	5	0.360	0.250	10				0.884	0.18	29.100	10.100		1.23	1.54	6.5	7.7
D	Totals		1.560	1.210	70	390.0	24.42	6.26	24.063	6.17	27.800	6.436		41.20	45.38	6.2	6.4
E	Armec Amine/Emulsified Mineral Oil/MIBC-F65	1	0.600	0.600	16	405.78	25.41	6.26	13.638	3.36	27.100	7.480	4380 1270	21.58	20.27	6.2	5.9
E	Armec Amine/Mineral Oil/MIBC-F65	2	0.600	0.600	13				8.874	21.4	25.500	8.570		12.91	14.77	5.8	6.7
E	Armec Amine/Mineral Oil/MIBC-F65	3	0.600	0.600	10				6.828	1.68	16.500	8.200		6.58	11.13	3.8	6.5
E	Armec Amine/Mineral Oil/MIBC-F65	4	0.600	0.600	10				34.320	8.46	1.720	581		3.45	3.96	0.4	0.5
E	A208/MIBC-F65	5	0.600	0.600	6.5				0.398	0.10	25.800	9.760		0.58	0.75	5.9	7.3
E	Totals		3.000	3.000	55.5	405.78	25.41	6.26	63.848	15.73	12.100	4.010		45.10	50.88	2.8	3.2
FSW1	Armec Amine/Emulsified Mineral Oil/MIBC-F65 Amine/Oil	1	0.140	0.140	30	788.0	27.3	3.47	31.20	3.96	32.200	9.820	4540 1360	25.68	25.03	7.1	7.1
FSW2	Armec Amine/Emulsified Mineral Oil/MIBC-F65 Amine/Oil	1	0.140	0.140	30	769.2	26.7	3.47	26.20	3.41	35.700	10.500	4810 1440	21.63	21.23	7.4	7.3

⁽¹⁾pCi in flotation concentrate X100
ΣpCi in all output streams

⁽²⁾Concentration in flotation concentrate
feed concentration



K-608(10)(I-11)
7-7-92

Fig. 3-9. Attrition scrub with hydrogen peroxide

Table 3-6
Preliminary Attrition Scrub Test

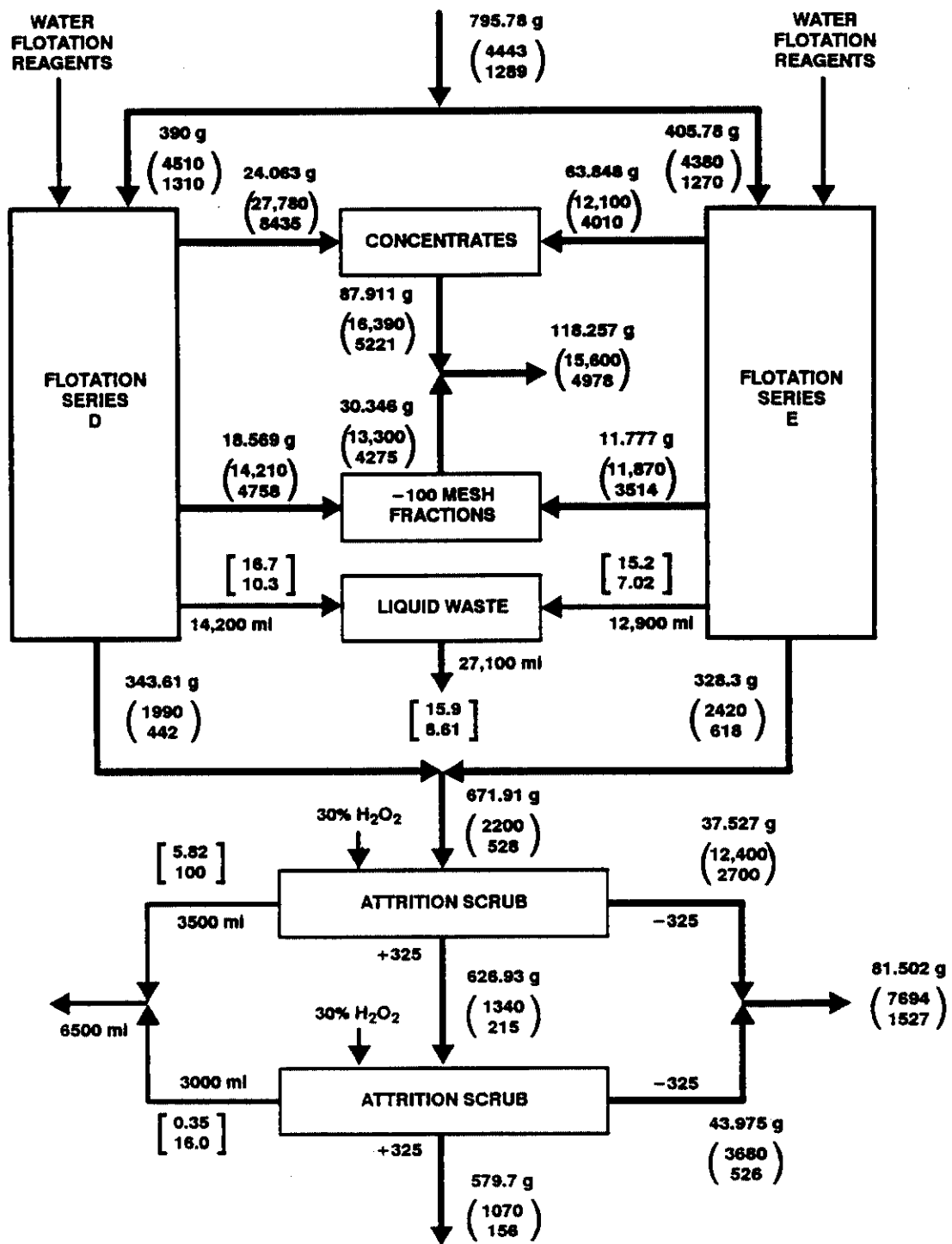
H₂O₂ Attrition Scrub Stage	Decontamination Factor⁽¹⁾ (% Contaminant reduction)⁽³⁾		Wt. Fraction -325 Mesh in Product	Percent Dissolved⁽²⁾	
	Cs-137	Co-60		Cs-137	Co-60
1	1.64 (39.1)	2.46 (59.3)	0.056	0.30	22.2
2	1.25 (20.1)	1.38 (27.4)	0.070	0.03	8.1
overall	2.06 (51.4)	3.38 (70.5)	0.121	---	---

- (1)
$$\frac{\text{Feed concentration}}{+325 \text{ Mesh Product Concentration}}$$
- (2) As a percentage of the total recovered
- (3)
$$\frac{(\text{Feed concentration} - \text{product concentration}) \times 100}{\text{feed concentration}}$$

lower Cs-137 and Co-60 concentrations than the +100 mesh fraction. This suggests that the attrition scrub product should be sieved to a size smaller than 100 mesh.

The combined flotation (Series D and E) and hydrogen peroxide attrition scrub process steps are illustrated in Figure 3-10 and summarized in Table 3-7.

Listed contaminant removal factors are based on removing the fines fractions, which have high Cs-137 and Co-60 concentrations, from the product stream after each major process step (flotation and attrition scrub). The ROD (Ref. 2) indicates a goal residual Cs-137 concentration of 690 pCi/g. Although the second stage attrition scrub product has a Cs-137 concentration a factor of 1.5 times higher than this goal, combining the treated product with the +4 mesh material in the original sample would yield an average Cs-137 concentration approaching the goal value.



K-608(9)(I-11)
7-7-92

Fig. 3-10. Preliminary flotation — attrition scrub summary

Table 3-7
Preliminary Flotation - Attrition Scrub
Result Summary

	Decontamination Factors ⁽³⁾ (% Contaminant Reduction) ⁽⁵⁾					
	Step		Cumulative		Fractional Fines Generated ⁽⁴⁾	
Process Step	Cs-137	Co-60	Cs-137	Co-60	Step	Cumulative
Flotation	2.02 ⁽¹⁾ (50.5)	2.44 ⁽¹⁾ (59.0)	2.02 (50.5)	2.44 (59.0)	0.149	0.149
1st Scrub	1.64 ⁽²⁾ (39.1)	2.46 ⁽²⁾ (59.3)	3.32 (69.8)	6.00 (83.3)	0.056	0.196
2nd Scrub	1.25 ⁽²⁾ (20.1)	1.38 ⁽²⁾ (27.4)	4.15 (75.9)	8.26 (87.9)	0.070	0.251

⁽¹⁾ $\frac{\text{Step feed concentration}}{\text{Step +100 mesh product concentration}}$

⁽²⁾ $\frac{\text{Step feed concentration}}{\text{Step +325 mesh product concentration}}$

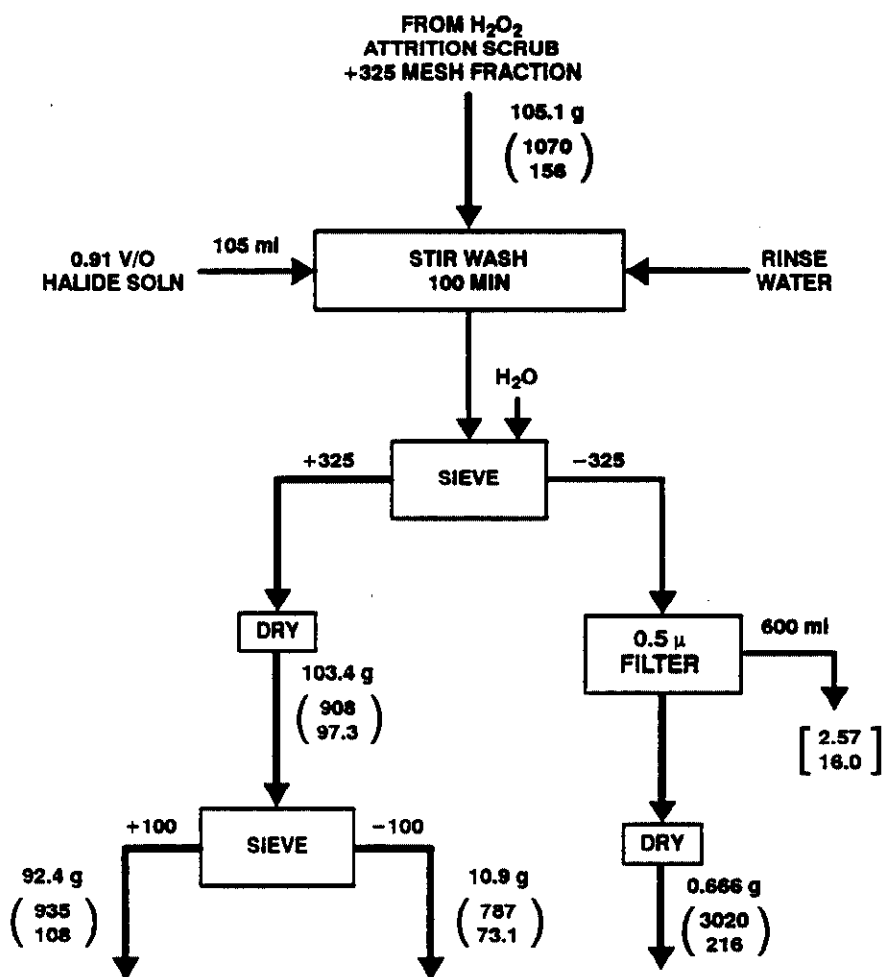
⁽³⁾ To achieve a Cs-137 level of 690 pCi/g, a Cs-137 DF of 6.44 is needed

⁽⁴⁾ Based on the feed quantity to the flotation step -- on the original sample basis, the fractional fines values are a factor of 2.1 lower

⁽⁵⁾ $\frac{(\text{Feed concentration} - \text{product concentration})}{\text{feed concentration}} \times 100$

3.2.4 Halide Treatment Test

A proprietary process application of a commercially available mixture of halides has been used successfully in the extraction of gold from gold ores. In application, an advantage of the halide process is the ability to regenerate and recycle the halide compound on-site. A portion of the hydrogen peroxide attrition scrub product was contacted with a solution of the proprietary halide mixture in a stir washer (manually stirring in a glass beaker). Test conditions and results are shown in Figure 3-11. Less than 0.5% of the residual Cs-137 dissolved, but 14% of the residual Co-60 did. The Cs-137 removal factor was low (DF of 1.18). Halide stir wash treatment offered no advantage over alternate stir wash treatments (see Table 3-4).



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7-2-92

Fig. 3-11. Halide treatment

As with the hydrogen peroxide attrition scrub product (Fig. 3-9), the halide treatment +325 mesh product was further sieved into a +100 mesh fraction and a -100 mesh fraction. Again the -100 mesh fraction was found to have lower residual Cs-137 and Co-60 concentrations than the +100 mesh fraction indicating the weight of material to low level waste can be further reduced by sieving at a finer mesh size.

3.2.5 Integrated Flotation Tests

Two integrated tests were made using the major process step sequence of flotation, sieving, single-stage attrition scrubbing, and stir washing. Feed for the tests came from the initial sample screening work (Fig. 3-1 and 3-2). The -4 mesh splits, 1 and 2 were combined, and split into seven aliquots. Separate aliquots were used for each test. The only prior processing these feed samples received was the initial coarse screening of the "as-received" sample.

Both tests, FSW-1 and FSW-2, utilized identical flotation processes. For attrition scrubbing, test FSW-1 used 30% hydrogen peroxide, whereas test FSW-2 used 0.74 M ammonium hydroxide. In both tests, the attrition scrub product was divided into three fractions, with each fraction subjected to different stir washing conditions (a total of six conditions). All particle size separations were done using a 100 mesh screen. Figures 3-12 and 3-13 present the test conditions and measurements¹ obtained for each test. Table 3-8 summarizes the test results.

Test FSW-1 flotation step had slightly higher Cs-137 and Co-60 removal factors than test FSW-2 but lower post-flotation sieving removal factors, resulting in about the same overall removal factors for the flotation-sieving combination. The feed sample was an aliquot of the -4 mesh portion of the original starting sediment sample. By comparison with the sample characterization values in Table 3-1B, the fines fraction and the contaminant removal factors agree well with those attainable by removal of the -325 mesh fraction. However, following the sieving at 100 mesh, the removal factors achieved and the fines fraction obtained were higher

¹Composition measurements of feeds to the stir wash steps were not made. Poor Cs-137 and Co-60 material balances for the individual test FSW-1 stir washes indicated feed composition variations occurred. The listed feed compositions were calculated from the weighted average product analyses.

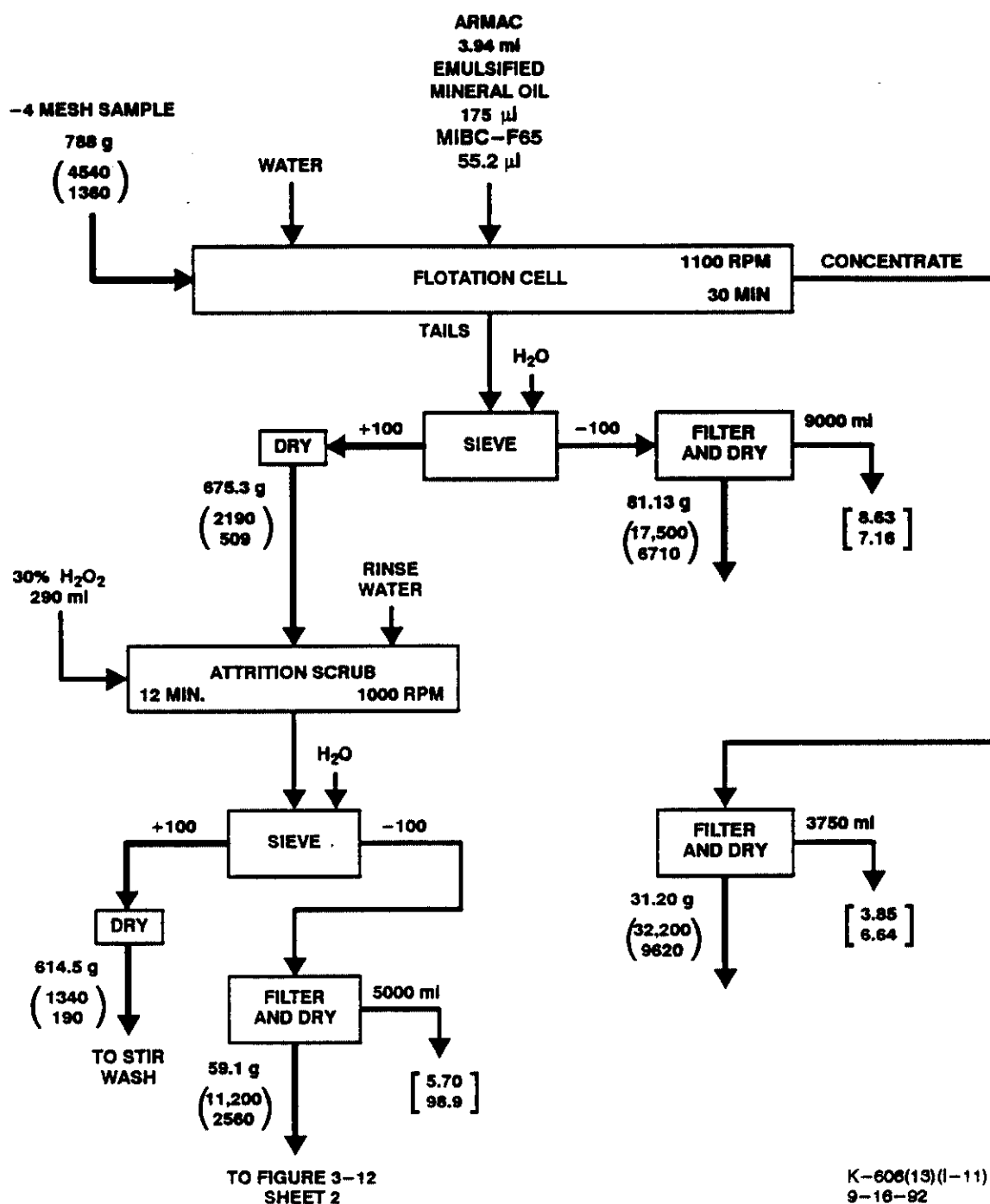


Fig. 3-12. (Sheet 1) Integrated test FSW-1 — flotation, sieving, and attrition scrub

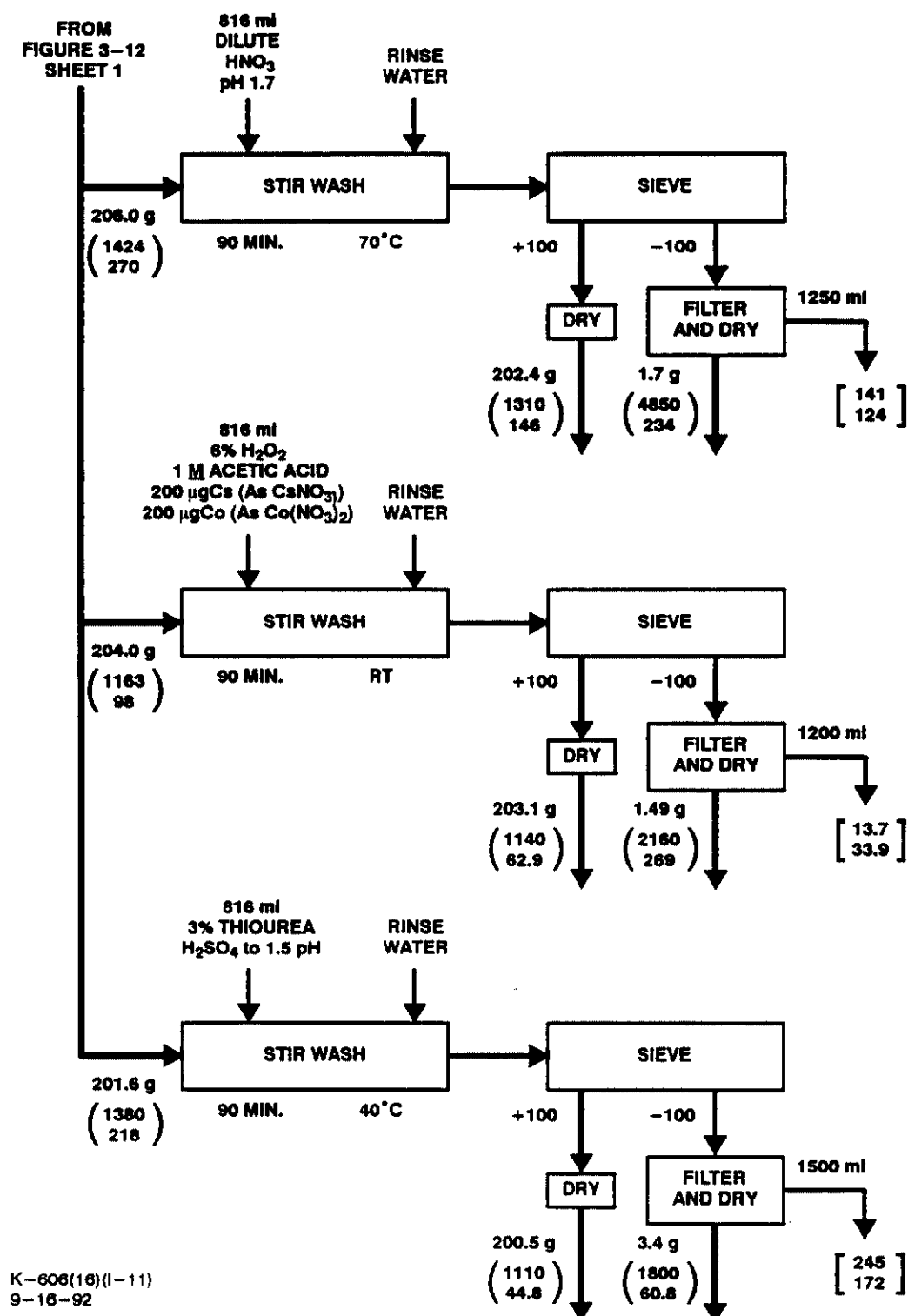


Fig. 3-12. (Sheet 2) Integrated test FSW-1 — stir washing

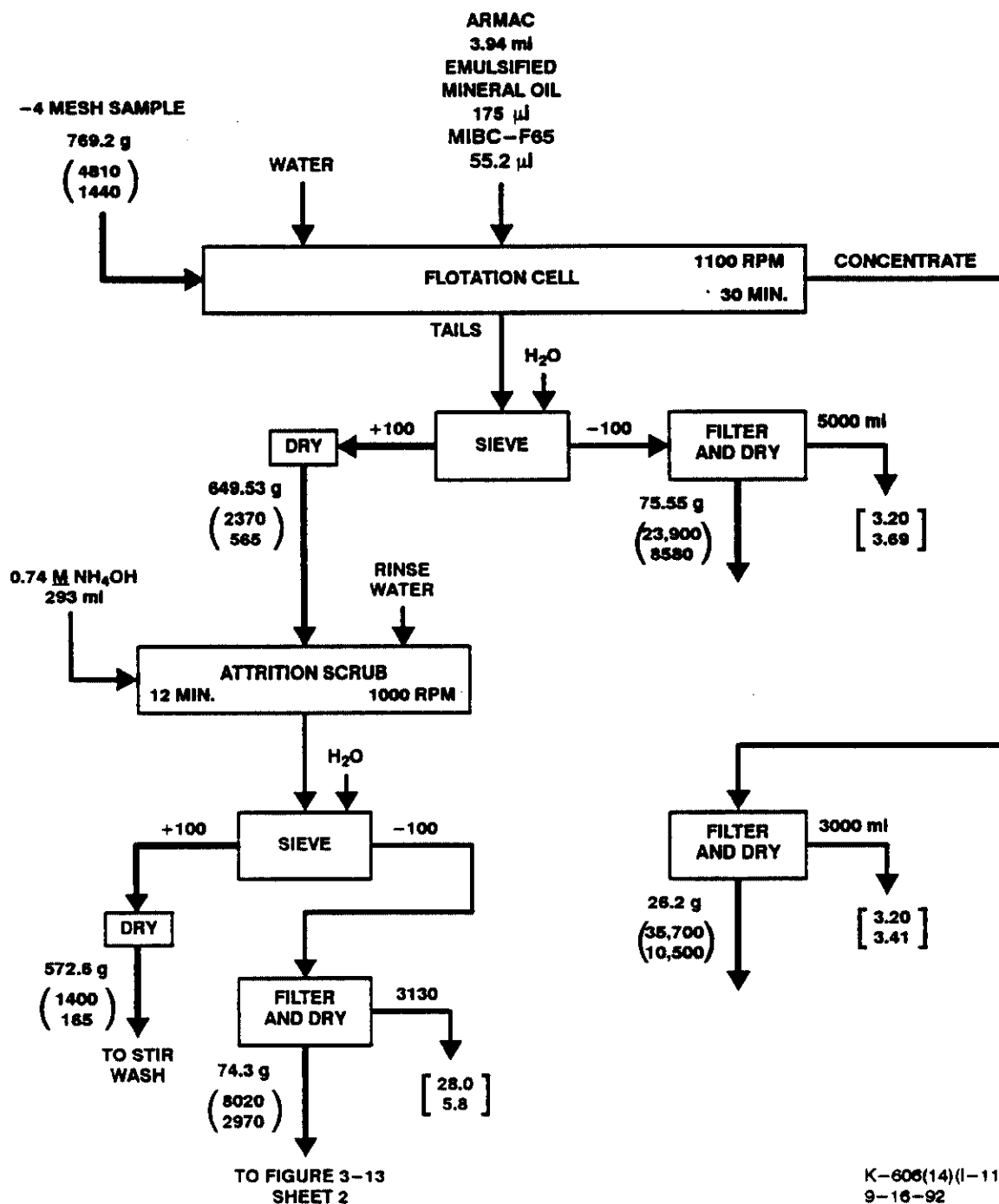


Fig. 3-13. (Sheet 1) Integrated test FSW-2 — flotation, sieving, and attrition scrub

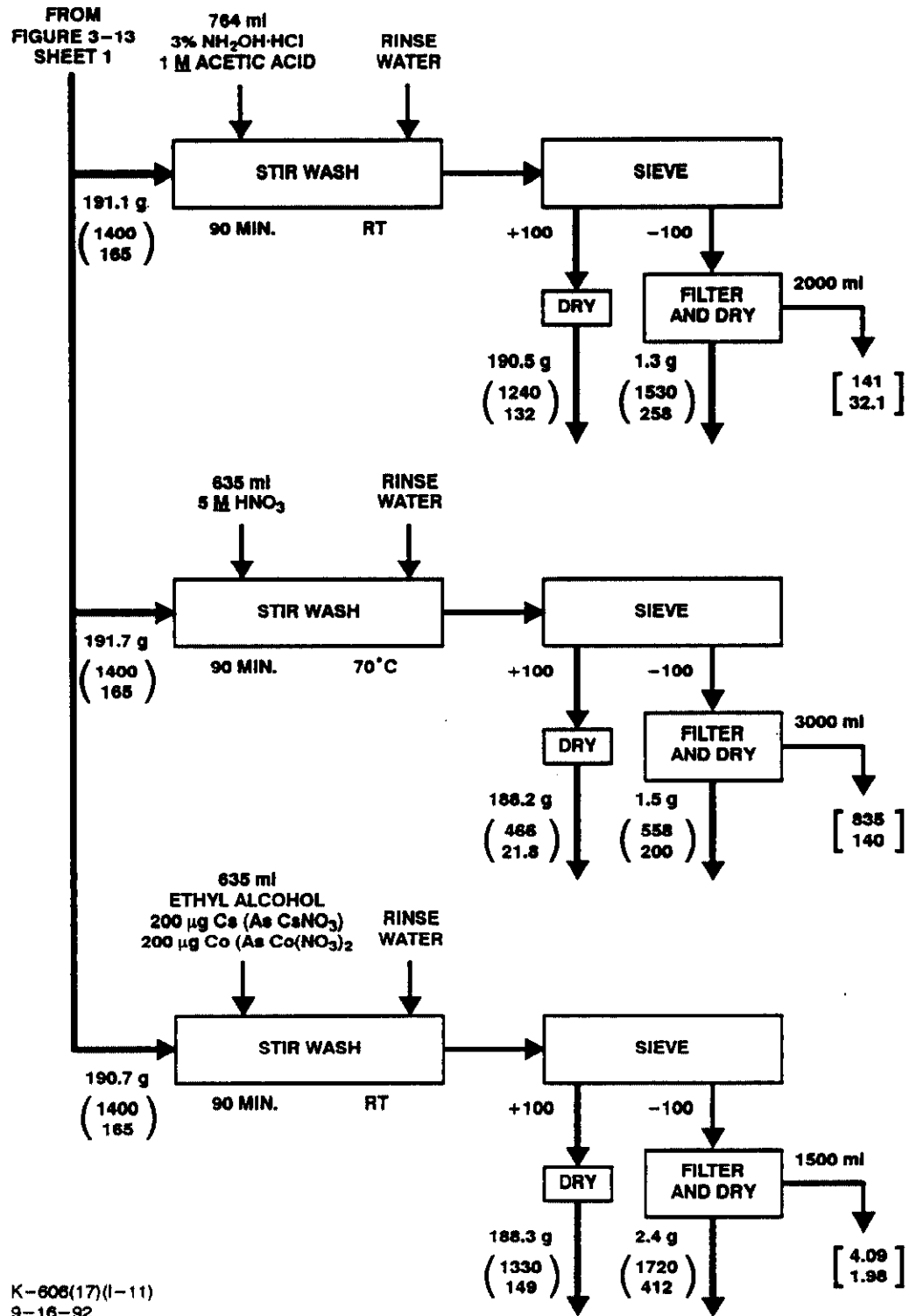


Fig. 3-13. (Sheet 2) Integrated test FSW-2 — stir washing

Table 3-8
Integrated Flotation Test Summary

	Decontamination Factor ⁽¹⁾⁽²⁾ (% Contaminant Reduction) ⁽³⁾				Fractional Fines Isolated		
	Step		Cumulative		Process Step	Cumulative ⁽⁵⁾	
Process Step	Cs-137	Co-60	Cs-137	Co-60		Test	Starting Sample
Test FSW-1							
Flotation	1.30 (23.1)	1.30 (23.1)	1.30 (23.1)	1.30 (23.1)	0.040	0.040	0.019
Sieving	1.75 (42.9)	2.31 (56.7)	2.27 (55.9)	2.99 (66.6)	0.107	0.143	0.067
H ₂ O ₂ Attrition Scrub	1.63 (38.7)	2.68 (62.7)	3.39 (70.5)	7.16 (86.0)	0.0875	0.218	0.103
Stir Washes ⁽⁴⁾							
Dilute HNO ₃	1.09 (8.3)	1.85 (45.9)	3.68 (72.8)	13.2 (92.4)	0.008	0.224	0.105
Acetic Acid + H ₂ O ₂ ⁽⁶⁾	1.02 (2.0)	1.56 (35.9)	3.46 (71.1)	11.2 (91.1)	0.007	0.223	0.105
Thiourea	1.24 (19.4)	4.87 (79.5)	4.21 (76.2)	35 (97.1)	0.017	0.231	0.109
Test FSW-2							
Flotation	1.21 (17.4)	1.20 (16.7)	1.21 (17.4)	1.20 (16.7)	0.034	0.034	0.016
Sieving	1.95 (48.7)	2.48 (59.7)	2.35 (57.4)	2.98 (66.4)	0.104	0.132	0.062
NH ₄ OH Attrition Scrub	1.69 (40.8)	3.42 (70.8)	3.44 (70.9)	8.73 (88.5)	0.114	0.229	0.108
Stir Washes ⁽⁴⁾							
NH ₂ OH • HCl + Acetic Acid	1.13 (11.5)	1.25 (20.0)	3.88 (74.2)	10.9 (90.8)	0.007	0.234	0.110
5M HNO ₃ ⁽⁷⁾	3.00 (66.7)	7.57 (86.8)	10.3 (90.3)	66 (98.5)	0.008	0.235	0.110
Ethyl Alcohol ⁽⁶⁾	1.05 (4.8)	1.11 (9.9)	3.62 (72.4)	9.66 (89.6)	0.013	0.238	0.112

⁽¹⁾ Flotation DF is feed concentration divided by calculated tails solids concentration

⁽²⁾ To achieve a Cs-137 level of 690 pCi/g, a Cs-137 DF of 6.58 is needed for Test FSW-1 and 6.97 for Test FSW-2
⁽³⁾ $(1-1/DF) \times 100$

⁽⁴⁾ Cumulative values are based on one of the listed stir washes coupled with the flotation, sieving, and attrition scrub steps

⁽⁵⁾ Based on feed to the flotation step -- on the original starting sample basis, the values are a factor of 2.1 lower

⁽⁶⁾ Wash solutions contained CsNO₃ and Co(NO₃)₂. Cs = Co = 1 kg/ton

⁽⁷⁾ DFs based on feed concentration divided by total product solids (+100 mesh and -100 mesh) are Cs-137 = 3.00, Co-60 = 7.11, Cs-137 (Cum) = 10.3, and Co-60 (Cum) = 62

than those expected from the Table 3-1B characterization results. This suggests some attrition of the feed during flotation and/or sieving.

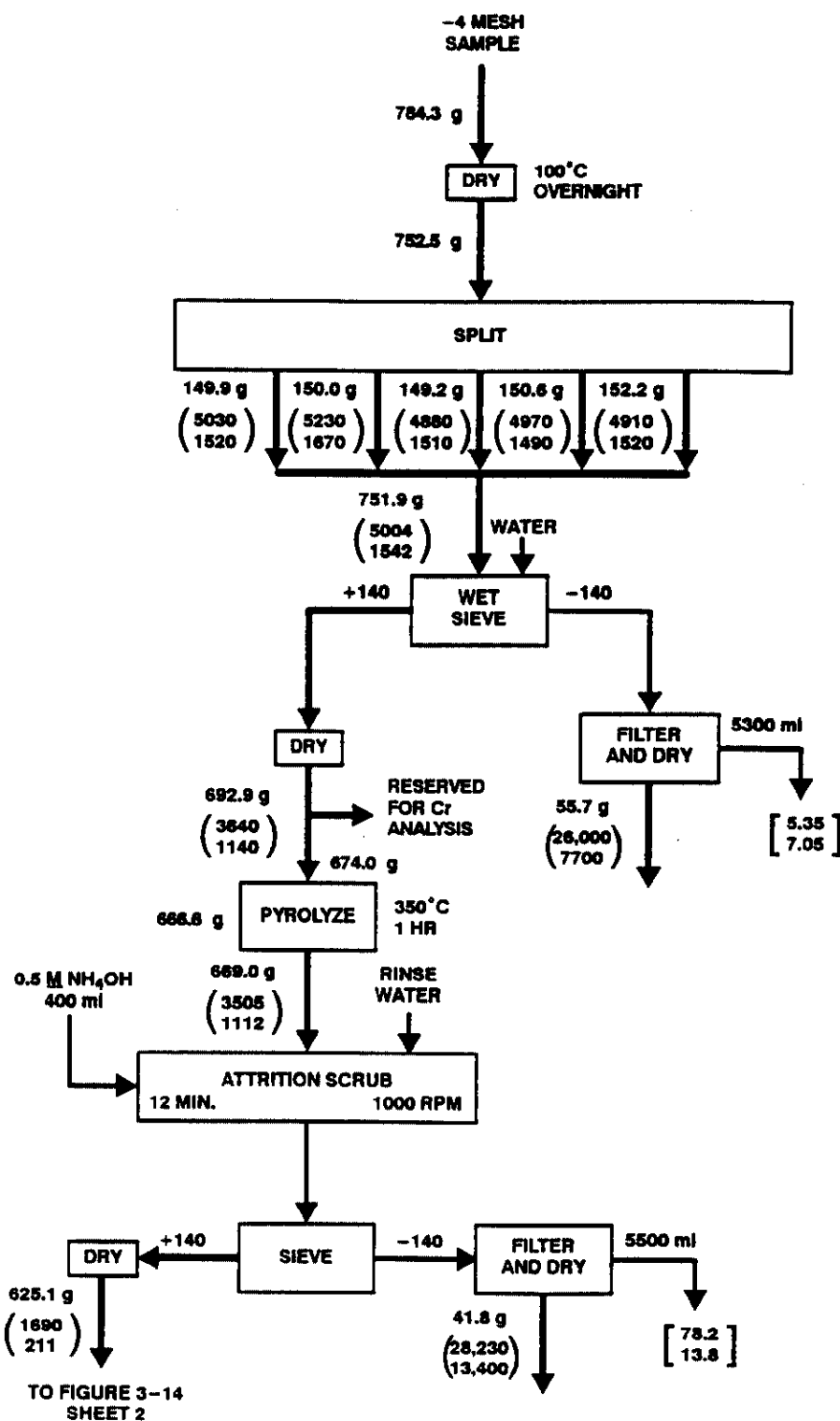
For attrition scrubbing, test FSW-1 used 30% hydrogen peroxide and test FSW-2 0.74 M ammonium hydroxide. The ammonium hydroxide yielded slightly better contaminant reduction, but generated more fines. Following attrition scrubbing, the +100 mesh products had residual Cs-137 concentrations twice the goal residual concentration of 690 pCi/g. Both of the attrition scrub products were split into three portions, with each portion stir washed with different reagents. In stir washing, the sediments were gently swirled by a mixer to just suspend the particles so as to minimize the formation of additional fines. Contamination removal was achieved principally by solubilizing the contaminants. Only 5 M nitric acid at 70°C reduced the Cs-137 concentration in the solid product to a concentration below the goal residual value of 690 pCi/g. This concentration could be achieved, even without a post-wash sieving step.

In two stir washes, cesium and cobalt nitrates were added for isotopic dilution of the radioactive species. Neither of these washes achieved significant contaminant reduction.

It should be noted that the Cs-137 and Co-60 material balances showed recoveries as much as 17% different from that contained in the feed. Contaminant removal factors based on a comparison to the total Cs-137 or Co-60 recovered could differ somewhat from those listed above. These differences, however, would not alter the conclusion concerning the effectiveness of the 5 M nitric acid stir wash.

3.2.6 Sieving Only Test with Pyrolysis

One integrated test (SPSW-1) was made using the major process sequence of sieving, pyrolysis, attrition scrubbing, and stir washing. Feed for the test was from the same source as that used for the integrated flotation tests. Sievings were made with 140 mesh screen (compared to 100 mesh for the integrated flotation tests) to reduce the quantity of fines requiring disposal as low-level waste. Figure 3-14 presents the test conditions and the measurements obtained. Table 3-9 contains a summary of the test results.



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Fig. 3-14. (Sheet 1) Integrated test SPSW-1 — sieving, pyrolysis, and attrition scrub

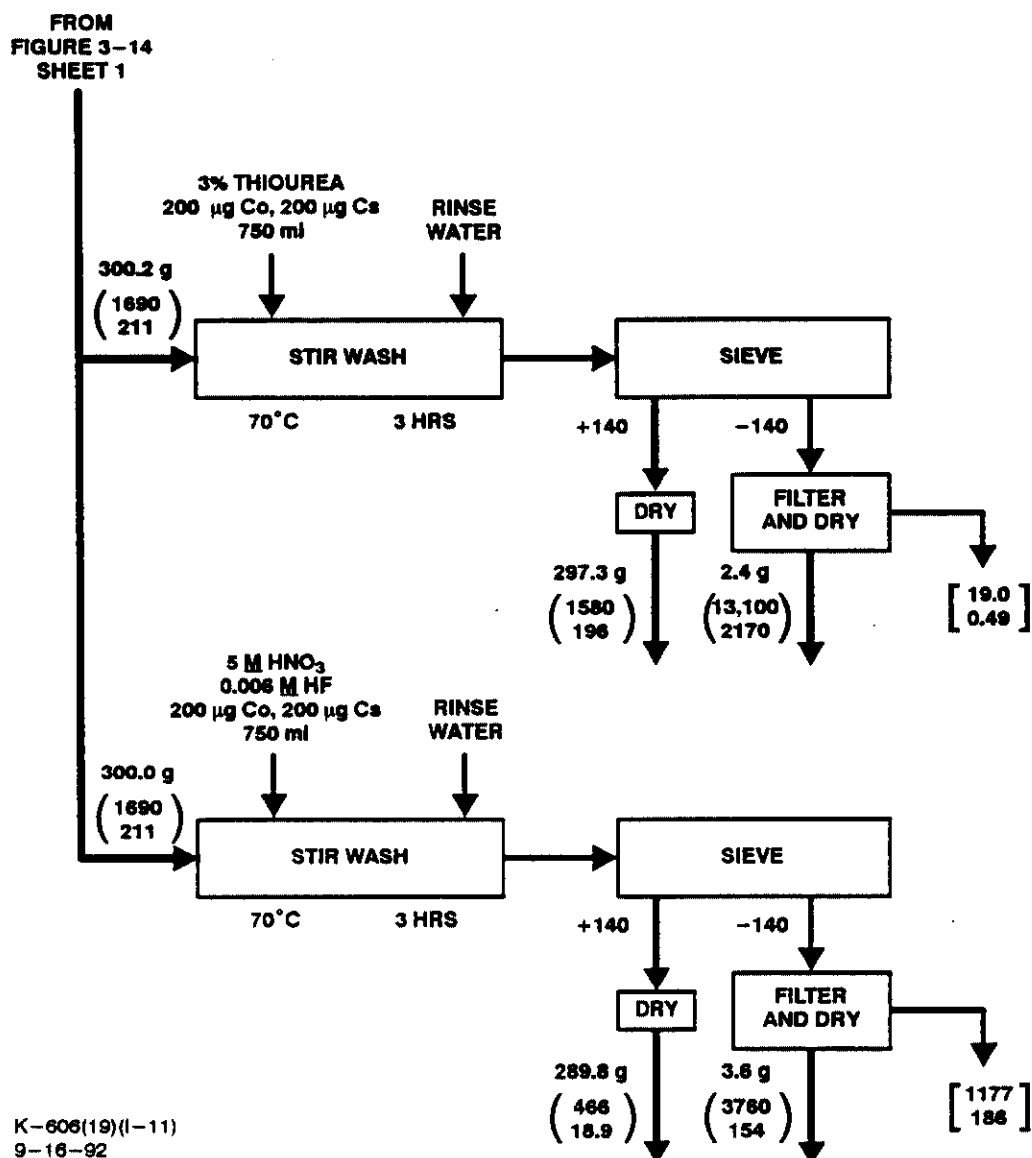


Fig. 3-14. (Sheet 2) Integrated test SPSW-1 — stir washing

Table 3-9
Sieve - Pyrolyze - Attrition Scrub - Stir Wash Summary
Test SPSW-1

	Decontamination Factor ⁽¹⁾⁽²⁾ (% Contaminant Reduction) ⁽³⁾				Fractional Fines Isolated		
	Step		Cumulative		Process	Cumulative ⁽⁵⁾	
Process Step	Cs-137	Co-60	Cs-137	Co-60	Step	Test	Starting Sample
Sieving	1.38 (27.3)	1.35 (26.1)	1.38 (27.3)	1.35 (26.1)	0.074	0.074	0.035
NH ₄ OH Attrition Scrub	2.07 (53.6)	5.27 (81.0)	2.96 (66.2)	7.31 (86.3)	0.063	0.130	0.061
Stir Washes ⁽⁴⁾							
3% Thiourea ⁽⁶⁾	1.07 (6.5)	1.08 (7.1)	3.16 (68.4)	7.87 (87.3)	0.008	0.136	0.064
5 M HNO ₃ ⁽⁶⁾⁽⁷⁾⁽⁸⁾	3.63 (72.4)	11.2 (91.0)	10.70 (90.7)	82 (98.8)	0.012	0.139	0.065

(1) Feed concentration divided by +140 mesh product concentration

(2) To achieve a Cs-137 level of 690 pCi/g, a Cs-137 DF of 7.25 is needed

(3) $\frac{(\text{Feed concentration} - \text{product concentration})}{\text{feed concentration}} \times 100$

(4) Cumulative values are based on one of the listed stir washes coupled with the sieving and attrition scrub steps

(5) Based on feed to the sieving step -- on the original starting sample basis, the values are a factor of 2.1 lower

(6) Wash solutions contained CsNO₃ and Co(NO₃)₂ -- Cs = Co = 0.7 kg/ton

(7) Also contained 0.006 M HF

(8) DFs based on feed concentration divided by total product solids (+140 mesh and -140 mesh) concentrations are Cs-137 = 3.34, Co-60 = 10.7, Cs-137 (Cum) = 9.9, and Co-60 (Cum) = 75

Overnight drying of the sample at 100°C resulted in a weight loss of 4.05%. A similar weight loss occurred in drying another -4 mesh sample split (Fig. 3-2) overnight at 60°C. This indicates that 60°C is an adequate temperature for drying the sediments to a constant moisture level. The dried sample was divided into five parts with a splitter and each part analyzed for Cs-137 and Co-60. The results indicate an uncertainty in sampling and analysis of about 3% for Cs-137 and 5% for Co-60.

Based on the initial sediment sample characterization (Table 3-1B), sieving at 140 mesh is expected to yield a -140 mesh fraction 5.56 wt% of the sieve feed. In the integrated test, the comparable -140 mesh fraction was 7.4 wt%. The sieving Cs-137 and Co-60 decontamination

factors based on feed and +140 mesh fraction concentrations were 1.38 and 1.35, respectively. These DFs are slightly lower than those anticipated from the sample characterization (Table 3-1-B). Feed sample differences and/or sieving and sampling reproducibility may account for the apparent discrepancies.

The dried +140 mesh fraction from the sieving steps was heated to 350°C and held for one hour to pyrolyze the organic material present. The sediments darken significantly during the pyrolysis. A 1.1 wt% loss occurred but, upon standing for a day, 0.39% of the lost weight was regained, presumably by moisture adsorption. Radiochemical analysis indicates some Cs-137 and Co-60 may have been lost during pyrolysis, but the apparent loss is within sampling/analytical error.

Attrition scrubbing/sieving of the pyrolyzed sediments with ammonium hydroxide yielded higher Cs-137 and Co-60 removal factors than those following flotation/sieving test FSW-2. However, the cumulative removal factors through attrition scrubbing were somewhat higher for the flotation/sieving/attrition scrubbing approach.

The attrition scrub +140 mesh product was divided into two parts and each part was subjected to a different stir wash. Three-hour stir washes were used instead of the 90-minute stir washes used with the flotation/sieve/attrition scrub +100 mesh products. Little contaminant removal was obtained with the 3% thiourea stir wash. In addition to time, this stir wash differed in two other aspects from the earlier thiourea stir wash: Isotopic dilution of the Cs and Co was used and the pH was not adjusted to 1.5 by sulfuric acid addition. The results indicate that isotopic dilution is of little, if any, benefit and acidification of the solution is important. It is also possible that the pyrolysis step had a detrimental effect on the thiourea stir wash.

As with the flotation/sieve/attrition scrub pretreatment, stir washing with 5 M nitric acid yielded products with acceptably low residual Cs-137 concentrations. After sieving, the larger fractions from tests FSW-2 and SPSW-1 had identical Cs-137 concentrations and nearly the same Co-60 concentrations. In both stir washes, the smaller fractions had low enough weight fractions that post-wash sieving was not needed to attain the goal residual Cs-137 concentration of 690 pCi/g. In both 5 M nitric acid stir washes, most of the Cs-137 and Co-60 present in the feed

was dissolved. In test SPSW-1, the 5 M nitric acid solution also contained low concentrations of Cs, Co, and HF. The effect of these additions is uncertain.

In comparing tests FSW-2 and SPSW-1 (with 5 M nitric acid), the overall contaminant reduction factors were similar. Test SPSW-1 attrition scrubbing and stir wash contaminant reduction factors were higher. It was not clear whether the higher reduction factors were due to including of the pyrolysis step, or to the higher starting Cs-137 and Co-60 concentrations from the lower pre-attrition scrub DFs. Test SPSW-1 yielded a significantly lower quantity of fines than test FSW-2 by almost a factor of two. Sieving at 140 mesh rather than 100 mesh undoubtedly was a major factor in the reduced fines yield.

Material balances for Cs-137 and Co-60 around the various test SPSW-1 process steps had recoveries as much as 6% different from the feed content. Contaminant reduction factors based on a comparison to the recovered values could differ somewhat from those listed above. These differences would not alter the conclusions concerning test SPSW-1.

Table 3-10 contains the details of selected attrition scrub and stir wash tests performed with Sample 1 sediments.

TABLE 3-10
SAMPLE 1 ATTRITION SCRUB AND STIR WASH TESTS

Test No.	Sample Fraction	Attrition Scrub Reagent	Stage	Reagent Strength	Scrub Solution (pH)	Reagent Temp (°C)	Contact Time (min.)	Pulp ⁽¹⁾ Density (%)	Post Treatment Sieving Mesh Size	wt. % Fines	pCl Cs-137/g		% ⁽²⁾ Reduction in CS-137	pCl Co-60/g		% Reduction in Co-60
											Initial	Final		Initial	Final	
Prelim.	12.25, 40 mesh	Sodium hydroxide	1	0.1 M NaOH	Basic	20	15	62.8	325	5.98	3.190	1.460	54.2	972	241	75.2
Prelim.	-4 mesh float. tail	Hydrogen peroxide	1	30% H ₂ O ₂	~ neutral	15-30	15	70.0	325	5.59	2.200	1.340	39.1	528	215	59.3
Prelim.	Scrub #1 residue	Hydrogen peroxide	2	30% H ₂ O ₂	~ neutral	15-25	15	70.0	325	7.01	1.340	1.070	20.1	215	158	27.4
FWS-1	+ 100 float. tail	Hydrogen peroxide	1	30% H ₂ O ₂	~ neutral	14-30.4	12	70.0	100	8.75	2.190	1.340	38.8	508	190	62.7
FWS-2	+ 100 float. tail	Ammonium hydroxide	1	0.74 M NH ₄ OH	10.8	20-25	12	68.9	100	11.44	2.370	1.400	40.9	565	165	70.8
SPSW-1	+ 140 screen pyrolysis	Ammonium hydroxide	1	0.5 M NH ₄ OH	10.5	20-25	12	62.6	140	6.25	3.505	1.690	51.8	1,112	211	81.0
		Stirred Wash Reagent														
Prelim.	+325, 2nd H ₂ O ₂	Proprietary halide	1	0.91 Vol %	pH 865 mv 1.6	20	100	50.0	325	0.63	1.070	908	15.1	158	97.3	37.6
FWS-1	+ 100 H ₂ O ₂	Dilute nitric	1	0.1 M HNO ₃	1.7	70	90	20.2	100	0.83	1.424	1.310	8.0	270	146	45.9
FWS-1	+ 100 H ₂ O ₂	Acetic acid/hydrogen peroxide/isotopic dilution	1	1 M HC ₂ H ₃ O ₂ 6% H ₂ O ₂	2.5	19.2	90	20.0	100	0.69	1.183	1.140	2.0	98	62.9	35.8
FWS-1	+ 100 H ₂ O ₂	Thiourea + H ₂ SO ₄	1	3% (NH ₂) ₂ CS	1.6	40	90	19.8	100	1.69	1.380	1.110	19.6	218	44.8	79.5
FWS-2	+ 100 NH ₄ OH	Hydroxylamine Hydrochloride/acetic acid	1	3% NH ₂ OH HCl 1 M HC ₂ H ₃ OH	2.6	18.4	90	20.0	100	0.68	1.400	1.240	11.4	165	132	20.0
FWS-2	+ 100 NH ₄ OH	Ethyl alcohol/isotopic dilution	1	Alcohol + 1 kg Cs. Co/t	--	19	90	23.1	100	1.3	1.400	1.330	5.0	165	149	9.7
FWS-2	+ 100 NH ₄ OH	Nitric acid	1	5 M HNO ₃	Low	70	90	23.2	100	0.78	1.400	466	66.7	165	21.8	86.8
SPSW-1	+ 140 NH ₄ OH + pyrolysis	Nitric acid/hydrofluoric/isotopic dilution	1	5 M HNO ₃ / 0.006 M HF	Low	70	180	28.6	140	1.20	1.690	468	72.4	211	18.9	91.0
SPSW-1	+ 140 NH ₄ OH + pyrolysis	Thiourea/isotopic dilution	1	3% (NH ₂) ₂ CS	--	70	180	28.6	140	0.80	1.690	1,580	6.5	211	196	7.1

⁽¹⁾ $\frac{\text{Feed weight} \times 100}{\text{feed weight} + \text{solution weight @ S.G.} = 1}$

⁽²⁾ $\frac{(\text{initial concentration} - \text{final concentration}) \times 100}{\text{initial concentration}}$

3.3 SECOND SAMPLE TESTS

After remediation testing of the first sample, additional samples were received for confirmatory testing of the remediation procedures developed with the first sample. The additional samples were from four different locations within the WWP. The samples were shipped in eight Type A DOT 7A containers with the following identifications:

<u>Container Number</u>	<u>Location</u>	<u>Location Number</u>
1	Cell 52 Corner 1	1
2	Cell 52 Center	3
3	Cell 52 Center	3
4	Cell 52 Corner 2	2
5	Cell 52 Corner 1	1
6	Cell 52 Corner 2	2
7	Cell 57 Corner	4
8	Cell 57 Corner	4

Reference 5 contains a copy of the sample documentation. Sample location numbers are shown in Fig. 1-1 and in Reference 5.

Initially containers 1 and 5 which held sediments from Cell 52 Corner 1 were selected for further testing because these containers had the highest external radiation level. An inspection revealed that this sample had a very high organic content (partially decayed and dried vegetation) and a very low gravel content. This material differed too radically from the first sample to be considered for confirmatory tests of procedures developed on the basis of the first sample composition. Containers 2 and 3, the samples from the center of Cell 52, were then selected because they most closely resembled the first sample in appearance. Verbal reports from NRT/ASI observers indicate that all eight samples in the four batches were taken with a common garden trowel, which would preclude their being collected at a depth of greater than approximately 4-6 inches deep. It is felt that Sample 2 is not representative of the soil data presented in Reference 1, but is likely representative of surface sediments.

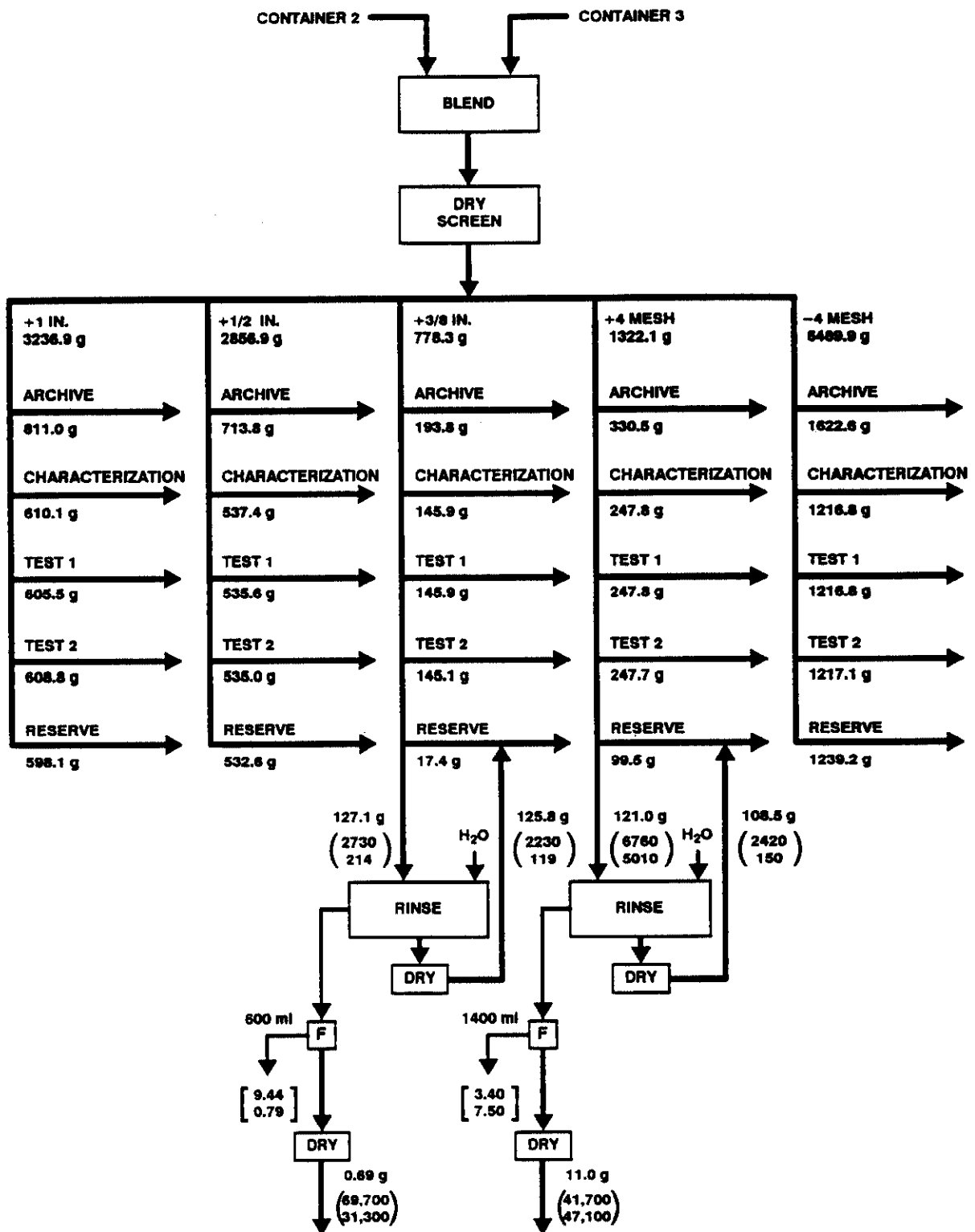
3.3.1 Sample Characterization

The contents of the two containers with the sediment sample from the center of Cell 52 were blended dry and screened into +1 inch, +½ inch, +¾ inch, +4 mesh, and -4 mesh fractions. The screening was necessary to divide the larger size fractions proportionately among the various sample splits. Figure 3-15 illustrates the splits made.

The sample was dry, raising dust during its handling. To minimize the loss of fine material and the spread of contamination, the characterization split was contacted with water in a rock polishing tumbler before wet sieving into the several mesh fractions. The fractions were then dried and analyzed as shown in Figure 3-16A, Sheet 1. Upon removal of the sample and water mix from the tumbler, some dried vegetation and rabbit dropping floated to the top, indicating a near surface origin as well as a relatively high organic content. Dried portions of the several --4 mesh fractions were then heated in a 400°C furnace overnight to determine weight loss on ignition, which would provide an estimate of their organic content. Figure 3-16A, Sheet 2 shows the measured weight losses. Several samples experienced weight losses in excess of 20%, indicating a high organic content.

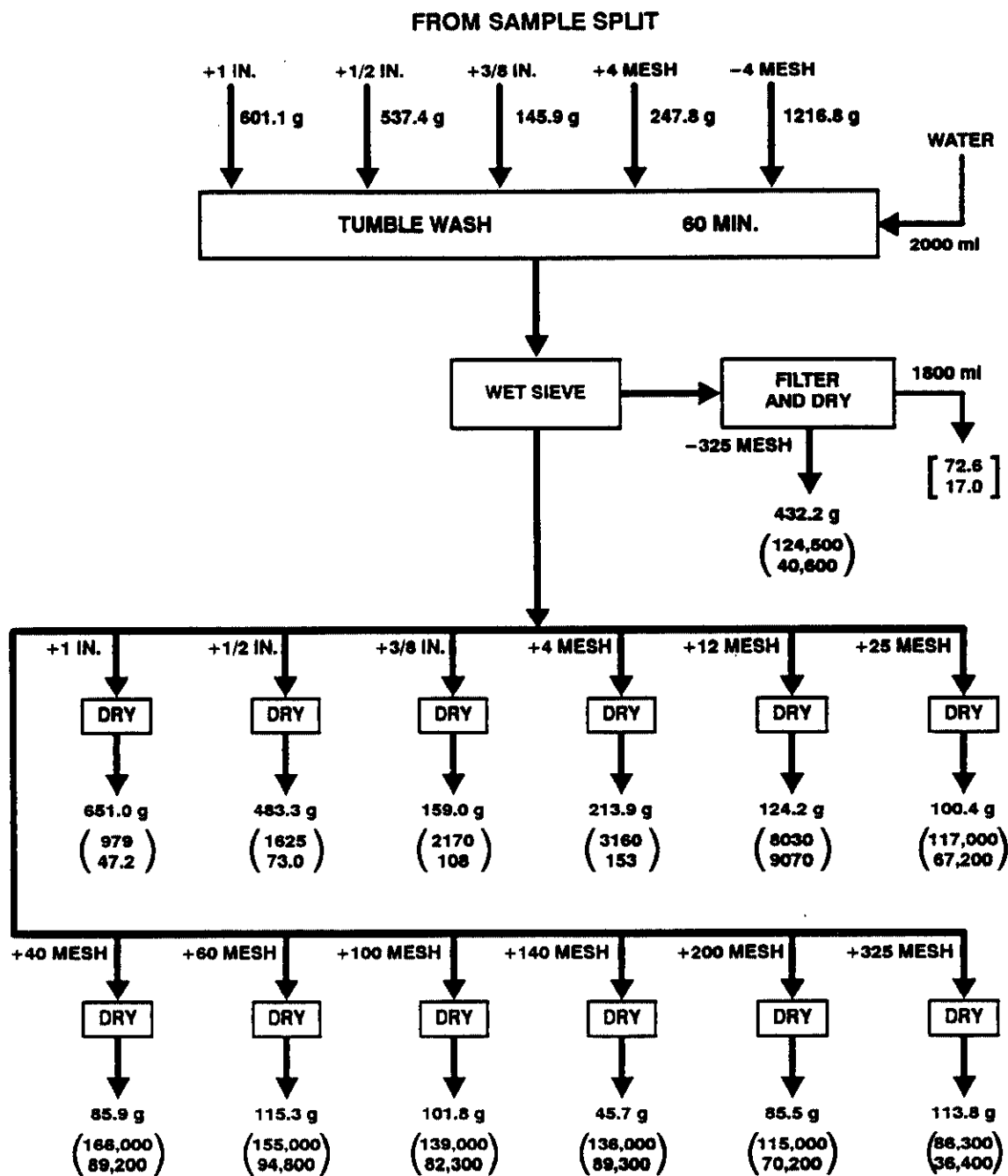
Ignition changed the second WWP sample color from dark brown and black to a sandy color. By contrast, the pyrolysis step in test SPSW-1 with the first WWP sample changed its color from sandy tan to dark brown and black.

Tables 3-11A and 3-11B summarize the characterization results. Cs-137 and Co-60 concentrations in the second sample are very much higher (more than 20 fold) than in the first sample, and more than 10 times the WWP averages (Ref. 1.) The higher organic content would appear to account for the higher radionuclide content. Table 3-11C contains a comparison of the two samples. In the first sample, the Cs-137 and Co-60 concentrations increased with decreasing particle size but, in the second sample, all fractions below 12 mesh had high concentrations with no significant trend. Both samples had comparable weight distributions of the +4 mesh fractions, but the second sample has significantly higher percentages of the fine mesh (-140 mesh) fractions. The organic content of the second sample is a factor of 10 higher than the first sample (8.6 weight % versus 0.75%).



K-606(20)(I-11)
8-24-92

Fig. 3-15. Second sample split



K-606(21)(I-11)
8-24-92

Fig. 3-16A. (Sheet 1) Second sample characterization sample sieving

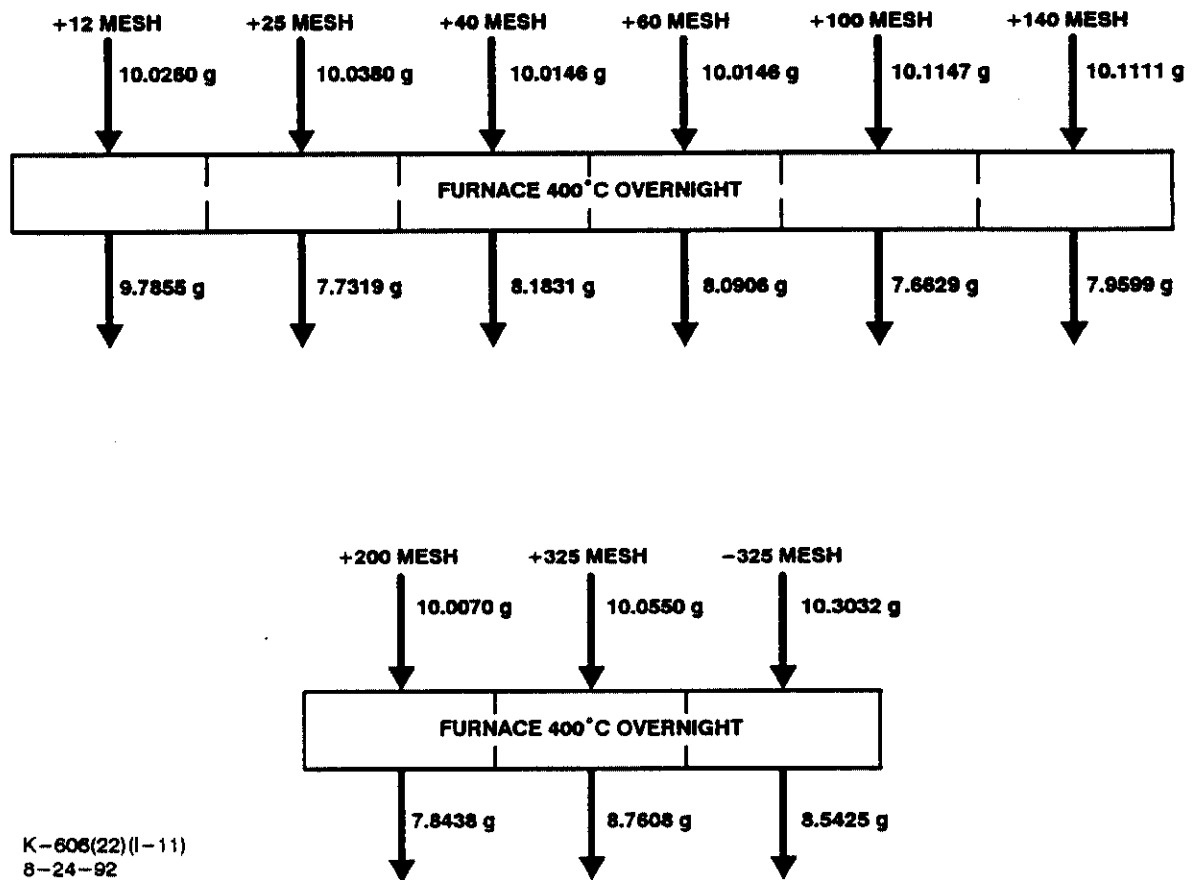


Fig. 3-16A. (Sheet 2) Second sample characterization – sample ignition

Table 3-11A
Second Sample Characterization Results - Large to Small

Retained Fraction	Weight, g		Analysis, pCi/g		Cumulative Average Concentration, pCi/g		Cumulative Percentages			Percent ⁽¹⁾⁽²⁾ Weight Loss on Ignition
	Fraction	Cumulative	Cs-137	Co-60	Cs-137	Co-60	Weight	Cs-137	Co-60	
1 inch	651.0	651.0	979	47.2	979	47.2	24.00	0.45	0.05	
½ inch	483.3	1134.3	1,625	73.0	1,255	58.2	41.83	1.01	0.10	
¾ inch	159.0	1293.3	2,170	108	1,370	64.3	47.69	1.25	0.12	
4 mesh	213.9	1507.2	3,160	153	1,620	76.9	55.58	1.73	0.17	
12 mesh	124.2	1631.4	8,030	9,070	2,110	761	60.15	2.44	1.86	2.40
25 mesh	100.4	1731.8	117,000	67,200	8,770	4,610	63.86	10.76	11.97	22.97
40 mesh	85.9	1817.7	166,000	89,200	16,200	8,610	67.02	20.86	23.45	18.28
60 mesh	115.3	1933.0	155,000	94,800	24,500	13,750	71.28	33.52	39.83	19.21
100 mesh	101.8	2034.8	139,000	82,300	30,200	17,200	75.03	43.55	52.39	24.24
140 mesh	45.7	2080.5	136,000	89,300	32,500	18,800	76.71	47.96	58.50	21.28
200 mesh	85.5	2166.0	115,000	70,200	35,800	20,800	79.87	54.92	67.49	21.62
325 mesh	113.8	2279.8	86,300	36,400	38,300	21,600	84.06	61.88	73.70	12.87
-325 mesh	432.2	2712.0	124,500	40,600	52,000	24,600	100.00	100.00	100.00	17.09

⁽¹⁾ At 400°C overnight

⁽²⁾ The weighted ignition losses are 17% for the -4 mesh portion and > 7.57% for the entire sample
The corresponding ignition losses for the first sample are 1.59% and 0.75%

Table 3-11B
Second Sample Characterization Results - Small to Large

Retained Fraction	Cumulative Percentages									
	Weight, g		Cumulative Average Concentration, pCi/g		Entire Sample			-4 Mesh		
	Fraction	Cumulative	Cs-137	Co-60	Weight	Cs-137	Co-60	Weight	Cs-137	Co-60
-325 mesh	432.2	432.2	124,500	40,600	15.94	124,500	40,600	35.87	38.80	26.34
325 mesh	113.8	546.0	116,500	39,700	20.13	116,500	39,700	45.32	45.88	32.56
200 mesh	85.5	631.5	116,300	43,800	23.29	116,300	43,800	52.42	52.96	41.56
140 mesh	45.7	677.2	177,700	46,900	24.97	117,700	46,900	56.21	57.45	47.70
100 mesh	101.8	779.0	120,400	51,500	28.72	120,400	51,500	64.66	67.65	60.27
60 mesh	115.3	894.3	124,900	57,100	32.98	124,900	57,100	74.23	80.53	76.67
40 mesh	85.9	980.2	128,500	59,900	36.14	128,500	59,900	81.36	90.84	88.18
25 mesh	100.4	1080.6	127,400	60,600	39.85	127,400	60,600	89.69	99.28	98.30
12 mesh	124.2	1204.8	115,100	55,300	44.42	115,100	55,300	100.00	100.00	100.00
4 mesh	213.9	1418.7	98,200	47,000	52.31	98,200	47,000			
¾ inch	159.0	1577.7	88,600	42,300	58.17	88,600	42,300			
½ inch	483.3	2061.0	68,200	32,400	76.00	68,200	32,400			
1 inch	651.0	2712.0	52,000	24,600	100.00	52,000	24,600			

Table 3-11C
Comparison of First and Second Sediment Samples

Fraction	Weight			Cs-137			Co-60		
	Percent			pCi/g			pCi/g		
	Sample 1	Sample 2	<u>Sample 2</u> Sample 1	Sample 1	Sample 2	<u>Sample 2</u> Sample 1	Sample 1	Sample 2	<u>Sample 2</u> Sample 1
1 inch	23.66	24.00	1.01	155	979	6.32	35	47.2	1.35
½ inch	13.58	17.82	1.31	504	1,625	3.22	112	73.0	0.65
¾ inch	5.17	5.86	1.13	712	2,170	3.05	146	108	0.74
4 mesh	10.46	7.89	0.75	897	3,160	3.52	191	153	0.80
12 mesh	8.49	4.58	0.54	1,150	8,030	6.98	218	9,070	41.6
25 mesh	7.82	3.70	0.47	3,020	117,000	38.7	887	67,200	75.8
40 mesh	13.85	3.17	0.23	4,070	166,000	40.8	1,290	89,200	69.1
60 mesh	9.49	4.25	0.45	3,710	155,000	41.8	1,030	94,800	92.0
100 mesh	3.72	3.75	1.01	5,480	139,000	25.4	1,800	82,300	45.7
140 mesh	0.99	1.69	1.71	10,200	136,000	13.3	4,140	89,300	21.6
200 mesh	0.44	3.15	7.16	15,300	115,000	7.52	5,680	70,200	12.4
325 mesh	0.55	4.20	7.64	20,000	86,300	4.32	6,270	36,400	5.81
-325 mesh	1.63	15.94	9.78	30,800	124,500	4.04	7,740	40,600	5.25
<u>Averages</u> Entire Sample	---	---	---	2,470	52,000	21.0	710	24,600	34.6
-4 mesh portion	47.05	44.42	0.94	4,750	115,100	24.2	1,400	55,300	39.5

Figure 3-16B graphically compares the particle size distributions of Samples 1 and 2 with the bounding and average (calculated) values contained in Reference 1. Sample 1 particle size distribution was close to the WWP average, but Sample 2 appeared to have a higher weight percent of fines than any of the Reference 1 characterization samples. This difference, however, may be due to the size measurement methodology. The Reference 1 measurements were apparently made by dry screening down to 200 mesh whereas Sample 1 and Sample 2 were wet screened down to 325 mesh. Wet screening appeared to break down agglomerates into finer particles with the attendant apparent increase in the fine fractions. Organic matter was likely an agglomerate binding agent. High organic content samples, such as Sample 2, would then have greater particle distribution disparities between wet and dry screening measurement methods.

Portions of the dry screened $+3/8$ inch and $+4$ mesh fractions were water washed, with Cs-137 and Co-60 measurements performed before and after washing (Fig. 3-15). Table 3-12 contains the results of the material removed by washing. More material, including radionuclides, was removed from the smaller size fraction, probably due to its higher surface area holding more fines. Comparable washings were not done with the $+1$ inch and $+1/2$ inch fractions because they had to be pulverized so their radionuclide content could be measured in the available spectrometer.

Table 3-12
Water Wash of $+3/8$ inch and $+4$ mesh Fractions

Decontamination Factor⁽¹⁾ (% Contaminant Reduction)⁽³⁾			
Fraction	Cs-137	Co-60	Weight Fraction Fines
$+3/8$ inch	1.22 (18.3)	1.80 (44.4)	0.005
$+4$ mesh	2.79 (64.2)	33.4 (97.0)	0.091

(1) Concentration before washing
Concentration after washing

(2) (Concentration before washing - concentration after washing) x 100
Concentration after washing

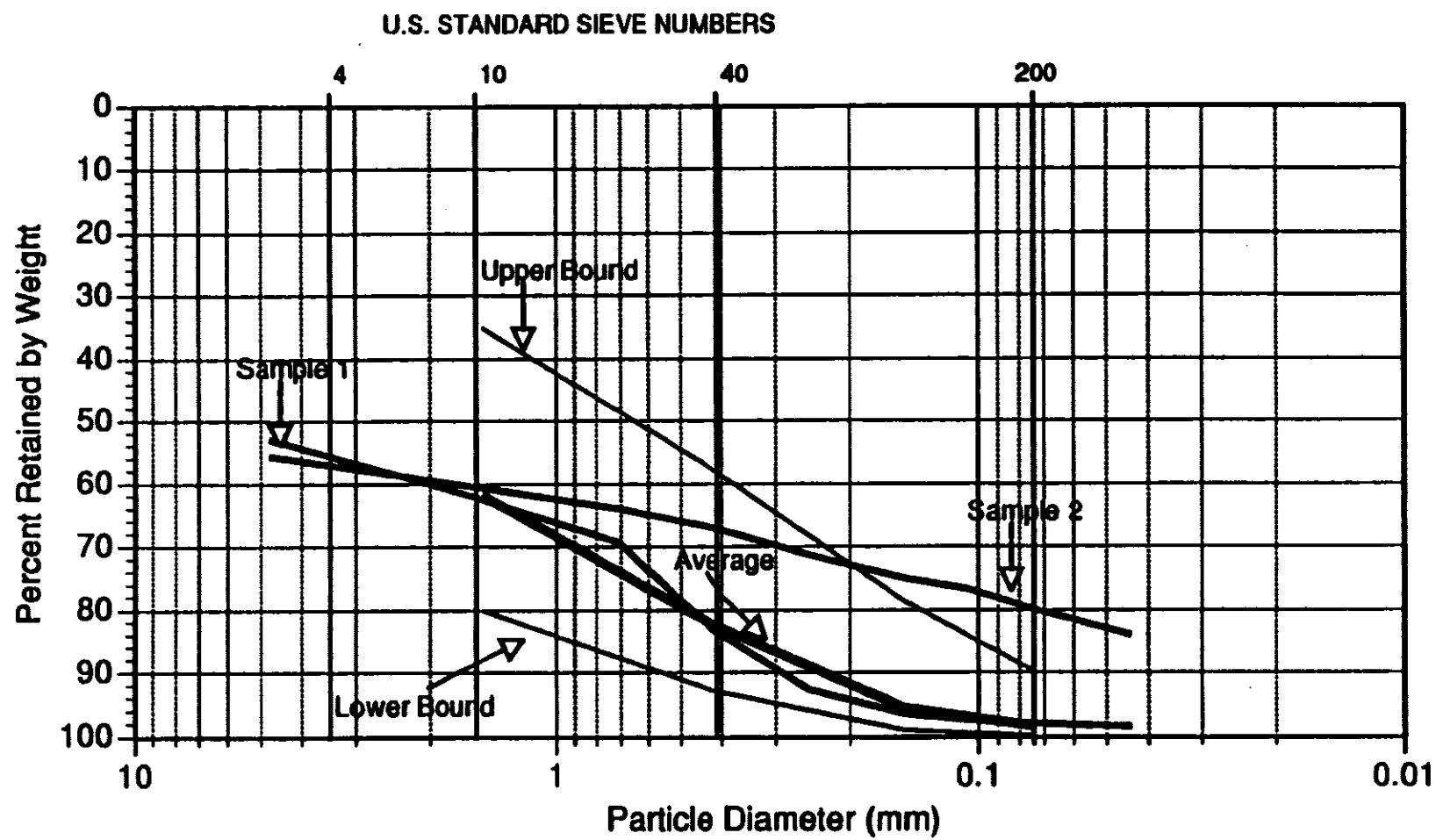


Fig. 16B. WWP sediment sample particle size comparison

3.3.2 Integrated Sieving Only Test (Test S2-1)

Test S2-1 was similar to Test SPSW-1 except that the pyrolysis step between the initial sieving and the attrition scrub was eliminated and the stir wash steps were slightly altered. Based on the sample characterization, the large mesh fractions (+4 mesh and above) also contained sufficient radioactive contamination to require treatment. Figure 3-17 (Sheets 1 and 2) contains the test conditions and the analytical results.

Large Mesh Fraction Treatment. The large mesh fractions (+1 inch, +½ inch, +¾ inch, and +4 mesh) received a two-stage treatment. First the fractions were soaked for three hours in 70°C 0.75 M ammonium hydroxide. This was followed by a 90-minute roll wash in 5 M nitric acid containing 0.01 M hydrofluoric acid. The roll washer consisted of a plastic bottle rolled horizontally on the rock tumbler drive. Because of the plastic bottles smooth interior, the rocks did not tumble. Table 3-13 summarizes the test results.

Neither treatment was effective in removing contaminants from the various fractions to acceptable values. Portions of the treated fractions still retained a partial coating of non-mineral (organic) material. It is likely the residual radioactivity is associated with this coating. Perhaps alternate treatment methods, such as vigorous tumbling and/or strong oxidation, would be more effective in removing this coating. Further investigation was outside the scope of this testing program.

Small Mesh Fraction Treatment. In the primary sieving steps for test S2-1, a split was made at 140 mesh similar to that used in the first sample sieving treatment (Test SPSW-1). With the second sample, more than half of the -4 mesh portion reported to the -140 mesh fraction. The Cs-137 and Co-60 split fairly evenly between the -140 mesh and +140 mesh fractions. The -140 mesh fraction was slightly enriched in Cs-137, while the +140 mesh fraction was enriched in Co-60. Table 3-14 compares the primary sieving operation performed on the two samples.

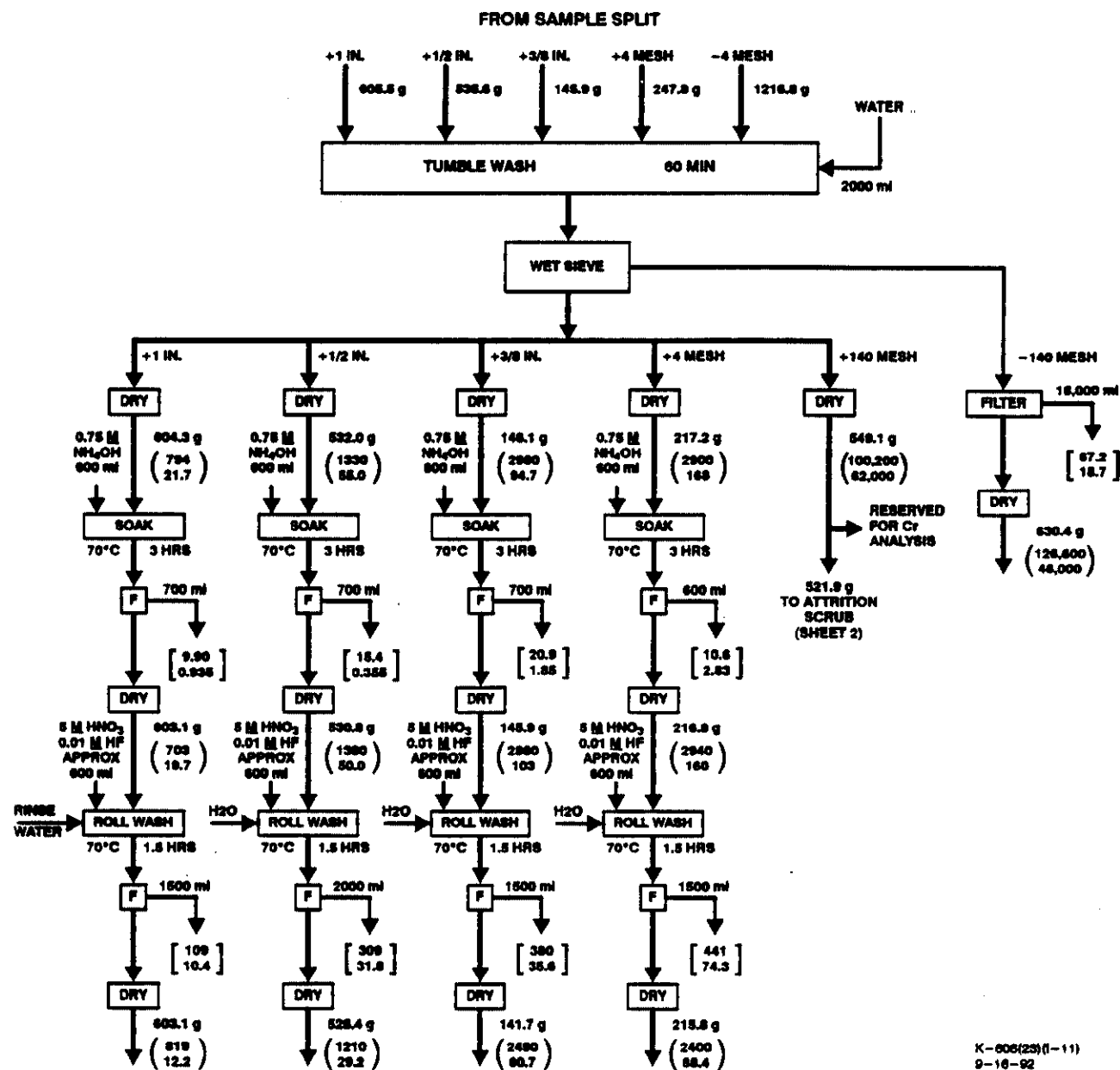


Fig. 3-17. (Sheet 1) Test S2-1 sieving and coarse fraction treatment

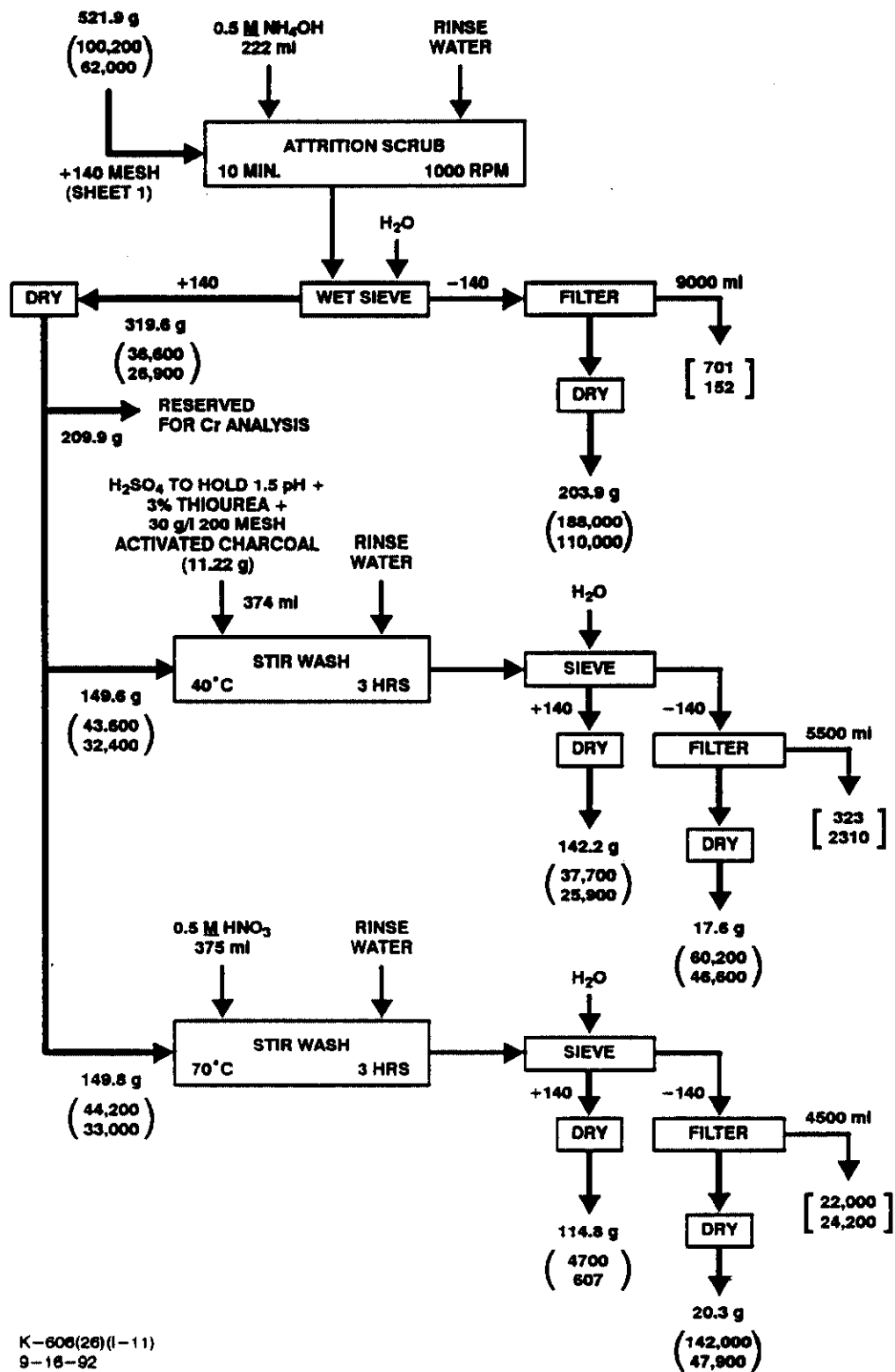


Fig. 3-17. (Sheet 2) Test S2-1 attrition scrub and stir washes

Table 3-13
Test S2-1
Treatment of +4 Mesh Fractions

Treatment	Fraction	Decontamination Factor ⁽¹⁾ (% Contaminant Reduction) ⁽²⁾			
		Step		Cumulative	
		Cs-137	Co-60	Cs-137	Co-60
NH ₄ OH Soak ⁽³⁾	+ 1 inch	1.13 (11.5)	1.10 (9.2)	1.13 (11.5)	1.10 (9.2)
	+ ½ inch	1.00 ⁽⁵⁾ (0)	1.10 (9.1)	1.00 ⁽⁵⁾ (0)	1.10 (9.1)
	+ ¾ inch	1.04 (4.0)	1.00 ⁽⁵⁾ (0)	1.04 (4.0)	1.00 ⁽⁵⁾ (0)
	+ 4 mesh	1.00 ⁽⁵⁾ (0)	1.05 (4.8)	1.00 ⁽⁵⁾ (0)	1.05 (4.8)
HNO ₃ Roll Wash ⁽⁴⁾	+ 1 inch	1.00 ⁽⁵⁾ (0)	1.61 (38.1)	1.00 ⁽⁵⁾ (0)	1.78 (43.8)
	+ ½ inch	1.14 (12.3)	1.71 (41.6)	1.10 (9.0)	1.88 (46.9)
	+ ¾ inch	1.15 (12.9)	1.70 (41.1)	1.20 (16.4)	1.56 (35.9)
	+ 4 mesh	1.23 (18.4)	1.81 (44.8)	1.21 (17.2)	1.90 (47.4)

⁽¹⁾ Feed concentration divided by product concentration

⁽²⁾ $\frac{(\text{Feed concentration} - \text{product concentration})}{\text{feed concentration}} \times 100$

⁽³⁾ Static soak in 70°C 0.75 M NH₄OH for 3 hours

⁽⁴⁾ Roll wash (no tumbling) in 70°C 5 M HNO₃ + 0.01 M HF for 1½ hours

⁽⁵⁾ Product sample had a higher value than feed -- a DF of 1.00 was assigned

Table 3-14
Comparison of First and Second Sample Sieving Operation

Sample	Decontamination Factor ⁽¹⁾ (% Contaminant Reduction) ⁽²⁾		Concentration Factor ⁽³⁾		Weight Fraction
	Cs-137	Co-60	Cs-137	Co-60	-140 Mesh ⁽⁴⁾
First	1.38 (27.3)	1.35 (26.1)	5.20	4.99	0.074
Second	1.14 (12.1)	0.86 (-)	1.11	0.86	0.534

⁽¹⁾ Feed (-4 mesh portion) concentration divided by +140 mesh fraction concentration

⁽²⁾ $\frac{(\text{Feed concentration} - \text{product concentration})}{\text{feed concentration}} \times 100$

⁽³⁾ Fines (-140 mesh fraction) concentration divided by -4 mesh portion concentration

⁽⁴⁾ Weight of -140 mesh fraction divided by feed weight

In contrast to the second sample, the first sample had relatively higher radionuclide concentrations in a relatively small weight fraction of fines. This permitted effective removal of radionuclides by sieving out the fines. Since all of the -12 mesh fractions in the second sample have high organic concentrations with high radionuclide content, a prescreening treatment to destroy the organic material would likely enhance subsequent radionuclide removal by sieving and/or dissolution.

Similar to Test SPSW-1 with sample 1, the +140 mesh fraction of sample 2 was attrition scrubbed with 0.5 M ammonium hydroxide, then sieved at 140 mesh. The appearance of the two attrition scrub products differed. In test SPSW-1, the product was a slurry, but in test S2-1, the product looked similar to wet concrete. Table 3-15 compares the two attrition scrubs. Of particular interest is the six-fold increase in the fines fraction produced by attrition scrubbing of the second sample. The ten-fold higher organic content was the likely cause of the fines increase. With the first sample, the Co-60 reduction factor was greater than that for Cs-137. With the second sample, the reverse was observed. The reason for this difference is unknown.

Table 3-15
Comparison of First and Second Sample Attrition Scrubbing
With Ammonium Hydroxide

Sample	Decontamination Factor ⁽¹⁾ (% Contaminant Reduction) ⁽²⁾		Concentration Factor ⁽³⁾		Weight Fraction -140 Mesh ⁽⁴⁾
	Cs-137	Co-60	Cs-137	Co-60	
First	2.07 (53.6)	5.27 (81.0)	8.05	12.05	0.063
Second	2.74 (63.5)	2.30 (56.6)	1.88	1.77	0.391

⁽¹⁾ Feed concentration divided by +140 mesh fraction concentration

⁽²⁾ $\frac{(\text{Feed concentration} - \text{product concentration})}{\text{feed concentration}} \times 100$

⁽³⁾ Fines (-140 mesh fraction) concentration divided by the feed concentration

⁽⁴⁾ Weight of -140 mesh fraction divided by feed weight

The +140 mesh fraction from the attrition scrub/sieving step was divided into two portions for separate stir wash treatments. One stir wash used a 3% thiourea solution acidified to pH 1.5

with sulfuric acid similar to that used in test FSW-1. In test S2-1, activated charcoal was also added to provide adsorption sites for radionuclides that may be solubilized but could be reabsorbed by the sediments. A 5 M nitric acid solution was used in the other stir wash (similar to test FSW-2 and SPSW-1).

Table 3-16 summarized the test results and presents a comparison with similar stir washes of the first sample. Although the stir wash of the second sample with the 5 M nitric acid yielded high contaminant reduction factors, the product fraction fell well short of the goal Cs-137 concentration because of the high starting concentrations. The high fractional fines from the second sample were likely related to its high initial organic content. Removal of the organic material before the stir wash would reduce the fractioned fines and perhaps further improve the contaminant reduction factors.

A comparison of tests S2-1 and FSW-1 thiourea stir washes indicated that the addition of the activated charcoal does not enhance contamination removal. In fact, the charcoal appeared to degrade the performance of the acidified thiourea. Acidification of the thiourea was of greater benefit to sediment cleaning than isotopic dilution, and 5 M nitric acid was much more effective than thiourea.

Table 3-17 summarizes the overall test S2-1 -4 mesh treatment results. The quantity of fines requiring disposal is excessive and the treated portion is well above the goal residual radionuclide concentrations. For these sediments, relatively high in organic material, an alternative treatment method is needed, or a pretreatment step could be added to destroy the organic material.

Table 3-16
Test S2-1 Stir Washes and Comparison to First Sample Stir Washes

Test No.	Stir Wash Conditions	Decontamination Factor ⁽¹⁾ (% Contaminant Reduction) ⁽³⁾		<u>Product Cs-137⁽³⁾</u> Goal Cs-137	Fines, Weight Fraction ⁽⁴⁾
		Cs-137	Co-60		
5M HNO ₃ Stir Washes					
S2-1	5M HNO ₃ , 70°C, 3 hours	9.40 (89.4)	54.4 (98.2)	6.81	0.136
FSW-2	5M HNO ₃ 70°C, 90 minutes	3.00 (66.7)	7.57 (86.8)	0.68	0.008
SPSW-1	5M HNO ₃ , 0.006M HF, trace Co(NO ₃) ₂ and CsNO ₃ , 70°C, 3 hours	3.63 (72.4)	11.2 (91.0)	0.68	0.012
3% Thiourea Stir Washes					
S2-1	3% thiourea, H ₂ SO ₄ to pH 1.5, 30 g/l 200 mesh activated charcoal, 40°C, 3 hours	1.16 (13.5)	1.25 (20.1)	55	0.109 ⁽⁵⁾
FSW-1	3% thiourea, H ₂ SO ₄ to pH 1.5, 40°C, 3 hours	1.24 (19.4)	4.87 (79.5)	1.61	0.017
SPSW-1	3% thiourea, trace Co(NO ₃) and CsNO ₃ , 70°C, 3 hours	1.07 (6.5)	1.08 (7.1)	2.29	0.008

⁽¹⁾ Feed concentration divided by product sieve fraction (+140 or +100 mesh) concentration

⁽²⁾ $\frac{(\text{Feed concentration} - \text{product concentration})}{\text{feed concentration}} \times 100$

⁽³⁾ Product sieve fraction Cs-137 concentration divided by goal Cs-137 concentration of 690 pCi/g

⁽⁴⁾ Smaller sieve fraction (-140 or -100 mesh) weight divided by stir wash feed weight

⁽⁵⁾ Includes added activated charcoal

Table 3-17
Test S2-1 Overall Results

Stir Wash Method	Overall Decontamination Factor ⁽¹⁾⁽³⁾ (% Contaminant Reduction) ⁽⁴⁾		Weight Fraction Fines ⁽²⁾
	Cs-137	Co-60	
5M HNO ₃	24.3 (95.9)	88.0 (98.9)	0.755
3% Thiourea	3.02 (66.9)	2.06 (51.9)	0.750

⁽¹⁾ Feed (-4 mesh) concentration divided by product concentration

⁽²⁾ Prorated fractional fines produced divided by -4 mesh fraction weight

⁽³⁾ To achieve the goal residual Cs-137 concentration of 690 pCi/g, an overall Cs-137 DF of 165 would be needed

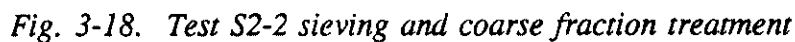
⁽⁴⁾
$$\frac{(\text{Feed concentration} - \text{product concentration})}{\text{feed concentration}} \times 100$$

3.3.3 Integrated Flotation Test (Test S2-2)

The protocol for second sample flotation test S2-2 was based on the procedures used in flotation tests FSW-1 and FSW-2 on the first sample. There were, however, some significant differences. A split of the entire second sample was used as feed material for test S2-2, rather than only -4 mesh portions used with the first sample flotation tests. After tumble washing, the test S2-2 feed was sieved into +1 inch, +½ inch, +¾ inch, +4 mesh, and -4 mesh fractions, with the -4 mesh fraction used as the flotation step feed. Figure 3-18 contains the process step used and the analytical results.

Large Mesh Fraction Treatment. The large fractions had Cs-137 concentrations above the goal concentration of less than 690 pCi/g (Ref. 2). Similar to test S2-1, the individual large fractions were treated for radionuclide removal as shown in Figure 3-18. First the individual fractions were soaked for three hours in 70°C 5 M nitric acid. Second, the fractions were roll washed in a 2% MICRO® solution for 90 minutes. MICRO® is a commercial detergent used for equipment decontamination in the Radiochemistry laboratory. Its Material Safety Data Sheet is contained in Reference 5. Table 3-18 lists the treatment results.

Some contaminant removal was achieved with the 5 M nitric acid soak, but the MICRO® roll wash did not achieve further removal. The treated fractions had a partial residual coating similar



to that described in paragraph 3.3.2 for the comparable test S2-1 fractions.

Small Mesh Fraction Treatment. The test S2-2 flotation treatment of the -4 mesh fraction differed in several respects from the tests FSW-1 and FSW-2 flotation treatments with the first sample. In tests FSW-1 and FSW-2, the flotation tails were sieved at 100 mesh before attrition scrub, but in test S2-2, the sieving step was omitted. Fines generated by test FSW-1 and FSW-2 attrition scrubbing were removed by sieving, but test S2-2 used a second flotation step. The same flotation reagents were used for all the integrated flotation tests. Figure 3-19 shows the test S2-2 flotation and attrition scrub tests.

Table 3-18
Test S2-2
Treatment of +4 Mesh Fractions

Treatment	Fraction	Decontamination Factor ⁽¹⁾ (% Contaminant Reduction) ⁽²⁾			
		Step		Cumulative	
		Cs-137	Co-60	Cs-137	Co-60
HNO ₃ soak ⁽³⁾	+ 1 inch	1.71 (41.5)	2.51 (60.1)	1.71	2.51
	+ ½ inch	1.54 (35.0)	2.10 (52.3)	1.54	2.10
	+ ¾ inch	1.95 (48.7)	2.39 (58.2)	1.95	2.39
	+ 4 mesh	1.78 (43.9)	2.67 (62.5)	1.78	2.67
MICRO roll wash ⁽⁴⁾	+ 1 inch	1.00 ⁽⁵⁾ (-)	1.12 (10.5)	1.68	2.80
	+ ½ inch	1.00 ⁽⁵⁾ (-)	1.00 ⁽⁵⁾ (-)	1.38	2.09
	+ ¾ inch	1.07 (6.6)	1.09 (8.6)	2.09	2.62
	+ 4 mesh	1.00 ⁽⁵⁾ (-)	1.17 (14.2)	1.68	3.11

⁽¹⁾ Feed concentration divided by product concentration

⁽²⁾ $\frac{(\text{Feed concentration} - \text{product concentration})}{\text{feed concentration}} \times 100$

⁽³⁾ Static soak in 70°C 5M HNO₃ for 3 hours

⁽⁴⁾ Roll wash (no tumbling) in 70°C 2% MICRO solution for 1½ hours

⁽⁵⁾ Product sample had a higher value than feed -- a DF of 1.00 was assigned

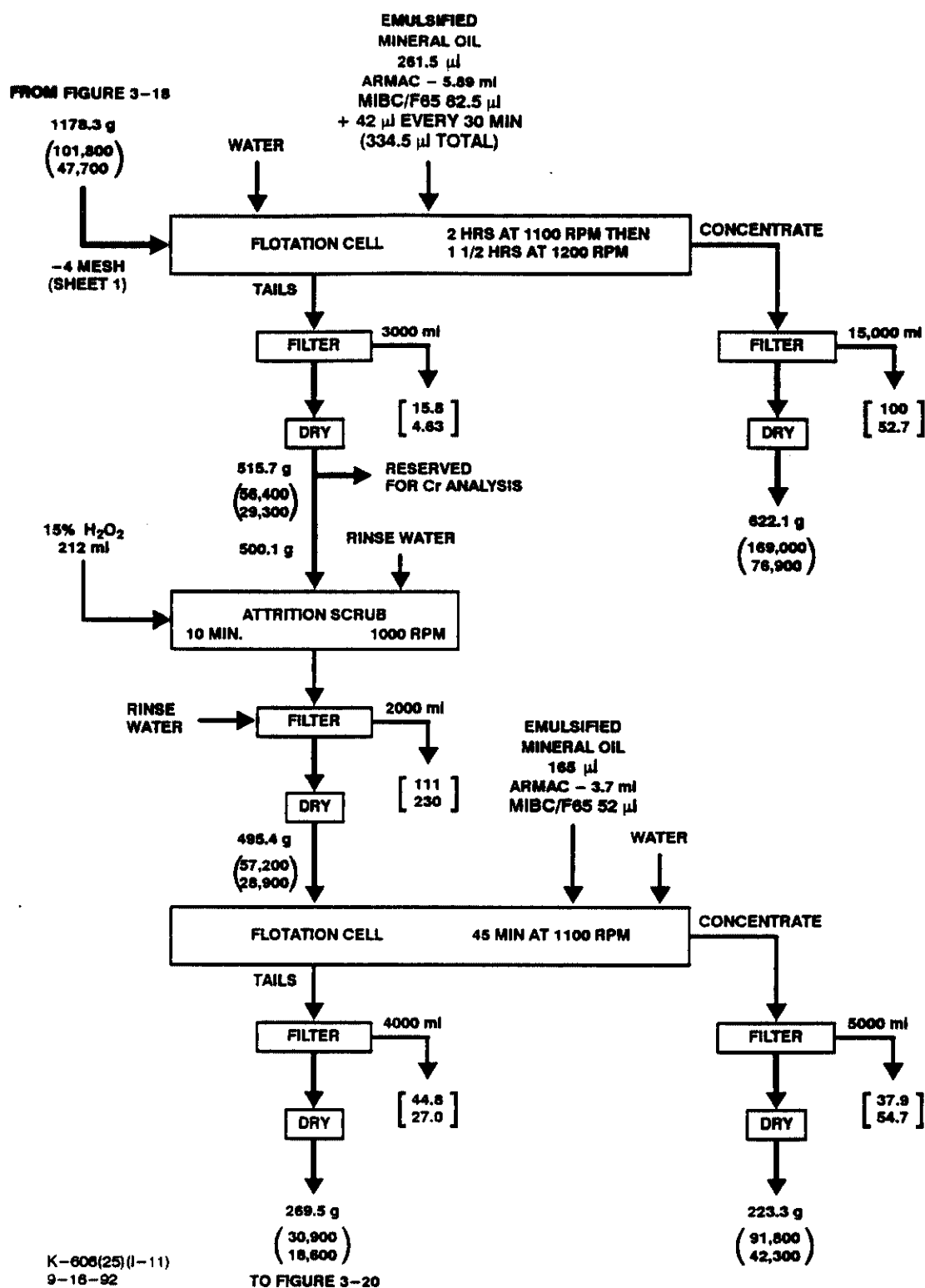


Fig. 3-19. Test S2-2 flotation and attrition scrub

Primary flotation with Sample 2 took considerably longer to complete than with Sample 1. Flotation was considered complete when the froth no longer appeared to contain a significant quantity of solids. Sample 2 flotation required 3½ hours compared to 30 minutes for Sample 1 flotations and produced a much greater quantity of concentrate. Table 3-19 summarizes the primary flotation results for the tests with both samples.

Table 3-19
Comparison of First and Second Sample Flotation Operations

Sample	Test No.	Decontamination Factor ⁽¹⁾ (% Contaminant Reduction) ⁽⁴⁾		Concentration Factor ⁽²⁾		Weight Fraction Concentrate ⁽³⁾
		Cs-137	Co-60	Cs-137	Co-60	
First	FSW-1	1.30 (23.1)	1.30 (23.1)	7.09	7.07	0.040
	FSW-2	1.21 (17.4)	1.20 (16.7)	7.42	7.29	0.034
Second	S2-2	1.80 (44.6)	1.63 (38.6)	1.66	1.61	0.528

⁽¹⁾ Feed concentration divided by tails concentration

⁽²⁾ Concentrate concentration divided by feed concentration

⁽³⁾ Weight of concentrate divided by weight of feed

⁽⁴⁾ $\frac{(\text{Feed concentration} - \text{product concentration})}{\text{feed concentration}} \times 100$

Sample 2 flotation yielded better contamination reduction, but an excessive quantity of fines (concentrate). With the high organic content second sample, more than half of the flotation feed reported to the concentrate stream. The high quantity of concentrate is also reflected in the low concentration factor attained with the second sample flotation. Compared to sieving (Table 3-14), flotation achieved better contamination reduction with comparable fractional fines production. The high organic material content would account for this difference. However, both methods generated an excessive quantity of fines with the second sample, indicating that a treatment step is needed to eliminate the organic material.

The test S2-2 attrition scrub step was similar to that used in test FSW-1, except that 15% hydrogen peroxide was used instead of 30%; the scrub time was reduced from 12 minutes to 10 minutes, and the attrition scrubbing generated fines were isolated by flotation instead of by

sieving at 100 mesh. Table 3-20 compares the two attrition scrub results. With the second sample, the Cs-137 reduction factor was slightly better, but the Co-60 reduction factor was much worse. Ammonium hydroxide attrition scrubbing gave similar results (Table 3-15). As usual, the amount of fines generated by the second sample was much greater than those from the first sample. Because of the great difference in organic content and size/radioactivity distribution (-12 mesh and below) between the two samples, little could be concluded as to which was the more efficient post-attrition scrub fines isolation method (sieving or flotation).

Table 3-20
Comparison of First and Second Sample Attrition Scrubbing with Hydrogen Peroxide

Sample	Decontamination Factor ⁽¹⁾ (% Contaminant Reduction) ⁽³⁾		Concentration Factor ⁽²⁾		Weight Fraction Fines ⁽⁴⁾
	Cs-137	Co-60	Cs-137	Co-60	
First ⁽⁵⁾	1.63 (38.7)	2.68 (62.7)	5.11	5.03	0.0875
Second ⁽⁶⁾	1.83 (45.2)	1.58 (36.5)	1.63	1.44	0.447

(1) Feed concentration divided by product concentration

(2) Fines concentration divided by feed concentration

(3) $\frac{(\text{Feed concentration} - \text{product concentration})}{\text{feed concentration}} \times 100$

(4) Weight of fines divided by weight of feed

(5) Used 30% hydrogen peroxide -- fines removed by sieving at 100 mesh

(6) Used 15% hydrogen peroxide -- fines removed by flotation

The tails from the post-attrition scrub flotation tails were split into two portions for separate final treatments. One treatment used pH 1.5 sulfuric acid solution in a stir wash contact (see Fig. 3-20). This acid concentration was the same as that used in the test FSW-1 and S2-1 thiourea stir washes. The two thiourea stir washes and the sulfuric acid stir wash are compared in Table 3-21. Better sediment contamination removal was obtained with sulfuric acid alone than with thiourea plus sulfuric acid.

The other post-attrition scrub flotation tails split was attrition scrubbed with a proprietary halide solution described in Section 3.2.4. Figure 3-20 illustrates the conditions and analytical results. Activated charcoal was added for the same reason described above for the thiourea stir wash. Table 3-22 lists the halide attrition scrub results.

Table 3-21
Comparison of Thiourea plus Sulfuric Acid and Sulfuric Acid Only Stir Washes

Test No.	Stir Wash Conditions	Decontamination Factor ⁽¹⁾ (% Contaminant Reduction) ⁽³⁾		Cs-137 ⁽²⁾ Product Goal Cs-137	Fines, Weight Fraction ⁽⁴⁾
		Cs-137	Co-60		
S2-2	pH 1.5 H ₂ SO ₄ , 40°C, 3 hours	2.45 (59.2)	2.27 (55.9)	44.8	0.186
S2-1	3% thiourea, H ₂ SO ₄ to pH 1.5, 30 g/l 200 mesh activated charcoal, 40°C, 3 hours	1.16 (13.5)	1.25 (20.1)	55	0.109 ⁽⁵⁾
FSW-1	3% thiourea, H ₂ SO ₄ to pH 1.5, 40°C, 90 minutes	1.24 (19.4)	4.87 (79.5)	1.61	0.017

⁽¹⁾ Feed concentration divided by product sieve fraction (+140 or +100 mesh) concentration

⁽²⁾ Produce sieve fraction Cs-137 concentration divided by goal Cs-137 concentration of 690 pCi/g

⁽³⁾ $\frac{(\text{Feed concentration} - \text{product concentration})}{\text{feed concentration}} \times 100$

⁽⁴⁾ Smaller sieve fraction (-140 or -100 mesh) weight divided by stir wash feed weight

⁽⁵⁾ Includes added activated charcoal

Table 3-22
Second Sample Attrition Scrub with Halide Solution

Test	Test Conditions	Decontamination Factor ⁽¹⁾ (% Contaminant Reduction) ⁽²⁾		Fines, Weight Fraction ⁽³⁾
		Cs-137	Co-60	
S2-2	0.9 v/o halide plus 30 g/l 200 mesh activated charcoal. Attrition scrub at 750 RPM. Run 5 minutes, add halide to eH > 750 mv. Repeat for run time of 15 minutes. Sieve at 100 mesh.	2.86 (65.0)	3.08 (67.5)	0.243 ⁽⁴⁾

⁽¹⁾ Feed concentration divided by +100 mesh product concentration

⁽²⁾ $\frac{(\text{Feed concentration} - \text{product concentration})}{\text{feed concentration}} \times 100$

⁽³⁾ Weight of -100 mesh fraction divided by weight of feed

⁽⁴⁾ Includes the added activated charcoal

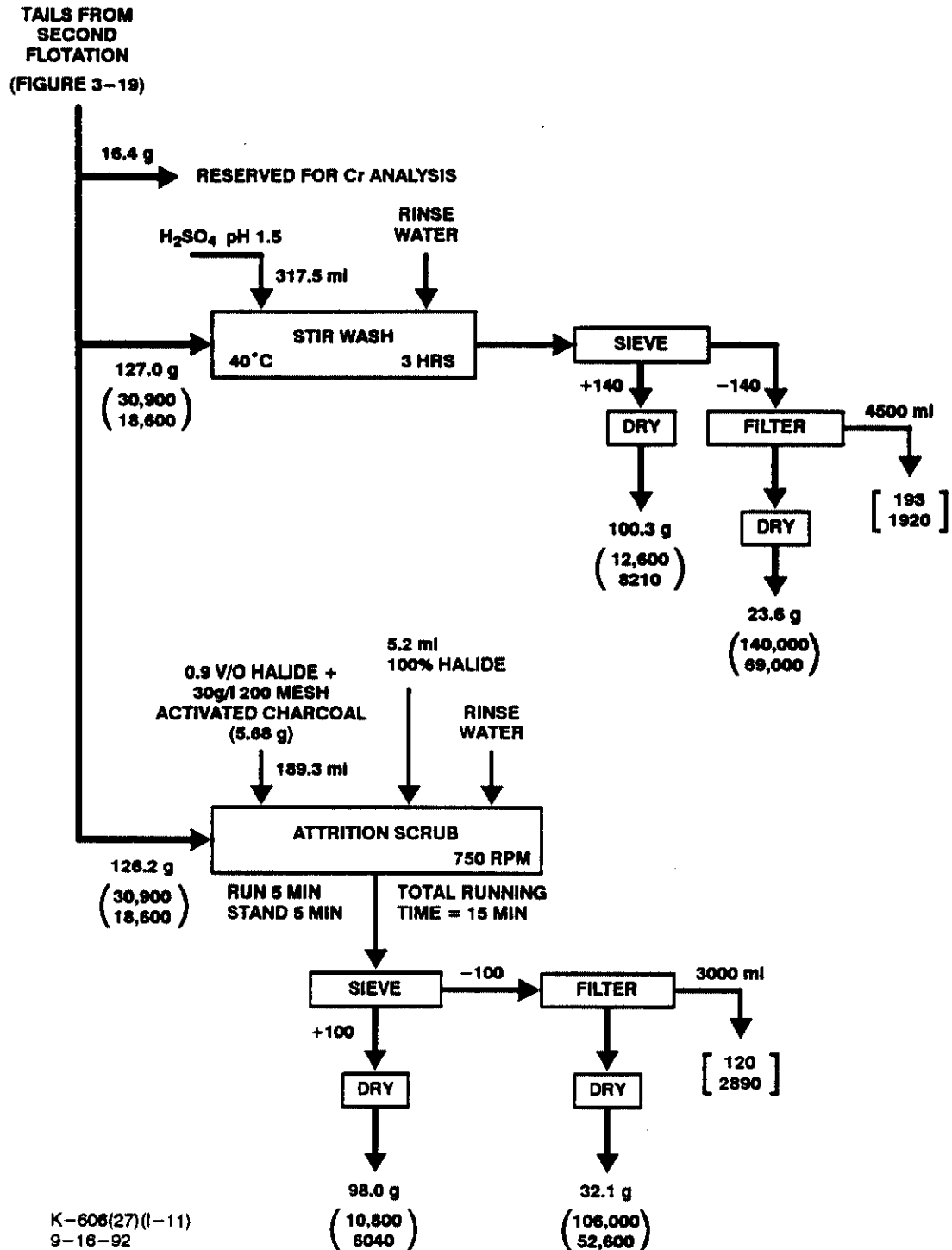


Fig. 3-20. Test S2-2 stir wash and final attrition scrub

The halide attrition scrub yielded better contaminant reduction factors than the sulfuric acid stir wash, but a higher weight fraction of fines requiring disposal.

Table 3-23 summarizes the overall test S2-2 treatment results of the -4 mesh fraction. As with test S2-1, the quantity of fines produced is excessive, and the treated portion has a Cs-137 concentration well in excess of the goal concentration.

Table 3-23
Test S2-2 Overall Results

Final Treatment Method	Overall Decontamination Factor ⁽¹⁾⁽²⁾ (% Contaminant Reduction) ⁽³⁾		Weight Fraction Fines ⁽⁴⁾
	Cs-137	Co-60	
H ₂ SO ₄ Stir Wash	8.08 (87.6)	5.81 (82.8)	0.767
Halide Attrition Scrub	9.43 (89.4)	7.85 (87.3)	0.783

⁽¹⁾ Flotation feed concentration divided by product concentration

⁽²⁾ To achieve the goal residual Cs-137 concentration of 690 pCi/g, an overall Cs-137 DF of 148 would be needed

⁽³⁾ $\frac{(\text{Feed concentration} - \text{product concentration})}{\text{feed concentration}} \times 100$

⁽⁴⁾ Prorated fractional fines produced divided by flotation feed weight

Table 3-24 contains a comparison of the four final treatments used in the two integrated tests with the second WWP sediment sample. Significantly higher contaminant reduction factors were attained with the 5 M nitric acid stir wash than with any of the other final treatments. This result agrees with the findings from the final treatment with the first sediment sample (Section 3.2). However, none of second sample final treatments yielded products with residual Cs-137 concentrations at or below the goal concentration.

Table 3-24
Second Sample Final Treatments

Final Treatment Method	Decontamination Factor ⁽¹⁾ (% Contaminant Reduction) ⁽²⁾		Fines, Weight Fraction ⁽³⁾
	Cs-137	Co-60	
Test S2-1 ⁽⁴⁾			
5 M HNO ₃ Stir Wash	9.40 (89.4)	54.4 (98.2)	0.136
3% Thiourea Stir Wash	1.16 (13.5)	1.25 (20.1)	0.109 ⁽⁵⁾
Test S2-2 ⁽⁴⁾			
pH 1.5 H ₂ SO ₄ Stir Wash	2.45 (59.2)	2.27 (55.9)	0.186
Halide Attrition Scrub	2.86 (65.0)	3.08 (67.5)	0.243 ⁽⁵⁾

⁽¹⁾ Concentration in feed to final treatment divided by product concentration

⁽²⁾ $\frac{(\text{Feed concentration} - \text{product concentration})}{\text{feed concentration}} \times 100$

⁽³⁾ Weight of fines divided by weight of feed to final treatment

⁽⁴⁾ Cs-137 decontamination factor needed to achieve the product goal concentration of 690 pCi/g is 64 for test S2-1 and 45 for test S2-2

⁽⁵⁾ Includes weight of activated charcoal added with reagent

3.3.4 Special Tests

After tests S2-1 and S2-2, the reserve split from the second sample (Figure 3-15) was dry screened into +1 inch, ½ inch, +¾ inch, +4 mesh, and -4 mesh fractions. These fractions were heated in a 400°C furnace for approximately 65 hours. Table 3-25 lists the measured weight losses of the various fractions resulting from burning and pyrolysis of the sediments. Following the furnace treatment, the +1 inch through +4 mesh fractions no longer had the partial coating of scum observed on the corresponding fractions after the chemical wash treatments of tests S2-1 and S2-2. However, some dark, finely divided material was present. The surface layer of the -4 mesh fraction was light in color, but dark material was noted underneath, suggesting incomplete combustion of the organic material. Further testing could include evaluation of means to improve organic oxidation. Additional testing was outside the scope of this test program.

Table 3-25
Second Sample Special Tests – Furnace Treatment Weight Loss

Fraction	Weights, g			Percent Weight Loss
	Initial	Final	Loss ⁽¹⁾	
+1 inch	598.1	593.5	5.0	0.84
+½ inch	532.2	527.3	4.9	0.92
+¾ inch	143.8	142.6	1.2	0.83
+4 mesh	208.1	205.1	3.0	1.44
-4 mesh	1230.6	1011.7	218.9 ⁽²⁾	17.79
	2712.8	2479.8	233.0	8.59

⁽¹⁾ At 400°C over a weekend

⁽²⁾ Organic material combustion not complete

Two aliquots of the heat treated -4 mesh fraction were stir washed. Table 3-26 lists the conditions and results. The stir wash slurries were filtered only with no prior sieving to remove fines. The listed contaminant reduction factors are due solely to solubilization of the Cs-137 and Co-60. The acetic acid-hydrogen peroxide mixture dissolved only a small fraction of the Cs-137 and Co-60, but the nitric acid dissolved an appreciable fraction. In appearance, the acetic acid-hydrogen peroxide filtrate was wine colored and the nitric acid filtrate black. These colors indicated incomplete oxidation of the organic material.

In the special test, a higher percentage of the Cs-137 was dissolved by the nitric acid than in test S2-1, but a smaller percentage than in the nitric acid stir washes with sample 1 sediments. This suggests more complete dissolution occurs in sediments with low organic content. Further testing would be needed if this relationship is to be clarified.

Table 3-26
Second Sample Special Test -- Stir Washing

Stir Wash Conditions	Decontamination Factor ⁽¹⁾ (% Contaminant Reduction) ⁽²⁾		Weight Loss, percent ⁽³⁾
	Cs-137	Co-60	
5M HNO ₃ + 0.025M HF ⁽⁴⁾	2.26 (55.7)	3.25 (69.2)	12.5
3M acetic acid (initial) + H ₂ O ₂ ⁽⁴⁾⁽⁵⁾ , Room temperature, 2 hours, pulp density 40% initial, 25% final	1.01 (0.8)	1.37 (27.1)	4.7

⁽¹⁾ Feed concentration divided by product concentration

⁽²⁾
$$\frac{(\text{Feed concentration} - \text{product concentration})}{\text{feed concentration}} \times 100$$

⁽³⁾ Feed-product weight difference divided by feed weight

⁽⁴⁾ Also contained 0.1g Cs (as CsNO₃) and 0.1g Co (as Co(NO₃)₂) per 100g of feed

⁽⁵⁾ 15% H₂O₂ added incrementally over 2 hour period

4.0 IMPLICATIONS FOR FUTURE REMEDIATION EFFORTS

The tests performed by NRT have demonstrated that Warm Waste Pond sediments with a low organic material content can be satisfactorily remediated with respect to WWP ROD requirements by combined physical and chemical means. Treatment options exist which minimize undesirable secondary wastes commonly associated with low pH, heated acid leaching of the sediment type which best represents most of the material under consideration for remediation. Surface sediments, however, not only contain very much higher Cs-137 and Co-60 concentrations, but also high organic material content. Sediments with high concentrations of organic material, alternate and/or additional processing steps are needed. Although the high organic surface sediments represent a small fraction (perhaps 10%) of the total WWP sediments to be remediated, it contains perhaps half of the Cs-137 and Co-60. Effective WWP remediation requires that appropriate means of processing the high organic, high contaminant sediments be addressed. A practical approach is to add a pretreatment operation for the high organic content sediments that would destroy the organic material, yielding a low organic material compatible with the processes for the bulk of the sediments (low organic subsurface sediments).

A possible method of organic destruction is by wet oxidation. Compared to dry oxidation, wet oxidation reduces the quantity of gaseous effluents requiring treatment and quantity of secondary wastes. Wet oxidation methods have been successfully employed on a production scale for the destruction of chemical agents and hazardous organic wastes for the U.S. military. A transportable wet oxidation unit has been built. Wet oxidation techniques developed for the military should be studied for application to high organic content WWP sediments and promising methods tested in the laboratory.

Vitrification offers an effective means for the fixation of radionuclides contained in nitrate salts. Additives required for vitrification include silica and carbon, both of which are contained in WWP sediments high in organic material. The possibility of disposing of the high organic

sediments during a nitrate salt vitrification processing may merit consideration and if judged feasible, appropriate testing could be undertaken.

Following the definition of workable treatment processes, pilot scale design, equipment selection and testing should be addressed.

5.0 REFERENCES

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